NOV 1 8 1930

Volume XXX November, 1930 Number 5

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

Relation of Nitrates in Soils to the Response of Crops to Potash Fertilization: I. Factors Contributing to the Unproductiveness of "Alkali" Soils in Illinois. O. H. Sears 325

The State of Unsaturation of the Soil in Relation to Its Field Behavior and Lime Requirement. P. E. Turner 349

The Decomposition of Lignified Materials by Soil Microörganisms. Max. Phillips, Herman D. Weihe, and N. R. Smith 383

The Determination of the Replaceable Bases and the Base-Exchange Capacity of Soils. H. D. Chapman and W. P. Kelley 391

Cross Inoculation with *Rhizobium radicicolum*. Victor Burke and Nelson J. Hohl 407

PUBLISHED MONTHLY
THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
Baltimore, Maryland, U. S. A.

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

Prof. A. W. Blair, Dr. J. S. Joffe, Prof. L. L. Lee, Dr. H. C. McLean, Dr. S. Mattson, Dr. J. W. Shive, Dr. R. L. Starkey and Dr. S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

DR. F. J. ALWAY
University of Minnesota, St. Paul, Minn.

PROF. K. ASO
Imperial University, Tokyo, Japan

PROF. C. BARTHEL
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa

PROF. DR. ALBERT DEMOLON
Ministry of Agriculture, Paris, France

DR. H. J. CONN
New York State Experiment Station, Geneva, N. Y.

DR. E. B. FRED
University of Wisconsin, Madison, Wis

DR. J. E. GREAVES
Utah Agricultural College, Logan, Utah

DIRECTOR ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium

DR. B. L. HARTWELL
Rhode Island Experiment Station, Kingston, R. I.

DR. D. J. HISSINK
Agricultural Experiment Station, Groningen, Holland

DR. C. B. LIPMAN
University of California, Berkeley, Calif.

DR. BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

DR. F. LÖHNIS
University of Leipsig, Germany

DR. T. L. LYON
Cornell University, Ithaca, N. Y.

DR. M. M. MCCOOL
Michigan State College, East Lansing, Mich.

DR. W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

DR. E. A. MITSCHERLICH
University of Königsberg, Prussia

PROF. C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

DR. SVEN ODÉN
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh.

PROF. G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy

DR. E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England

DR. O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.

DR. ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

DR. J. STOKLASA
Technical High School, Prague, Czechoslovakia

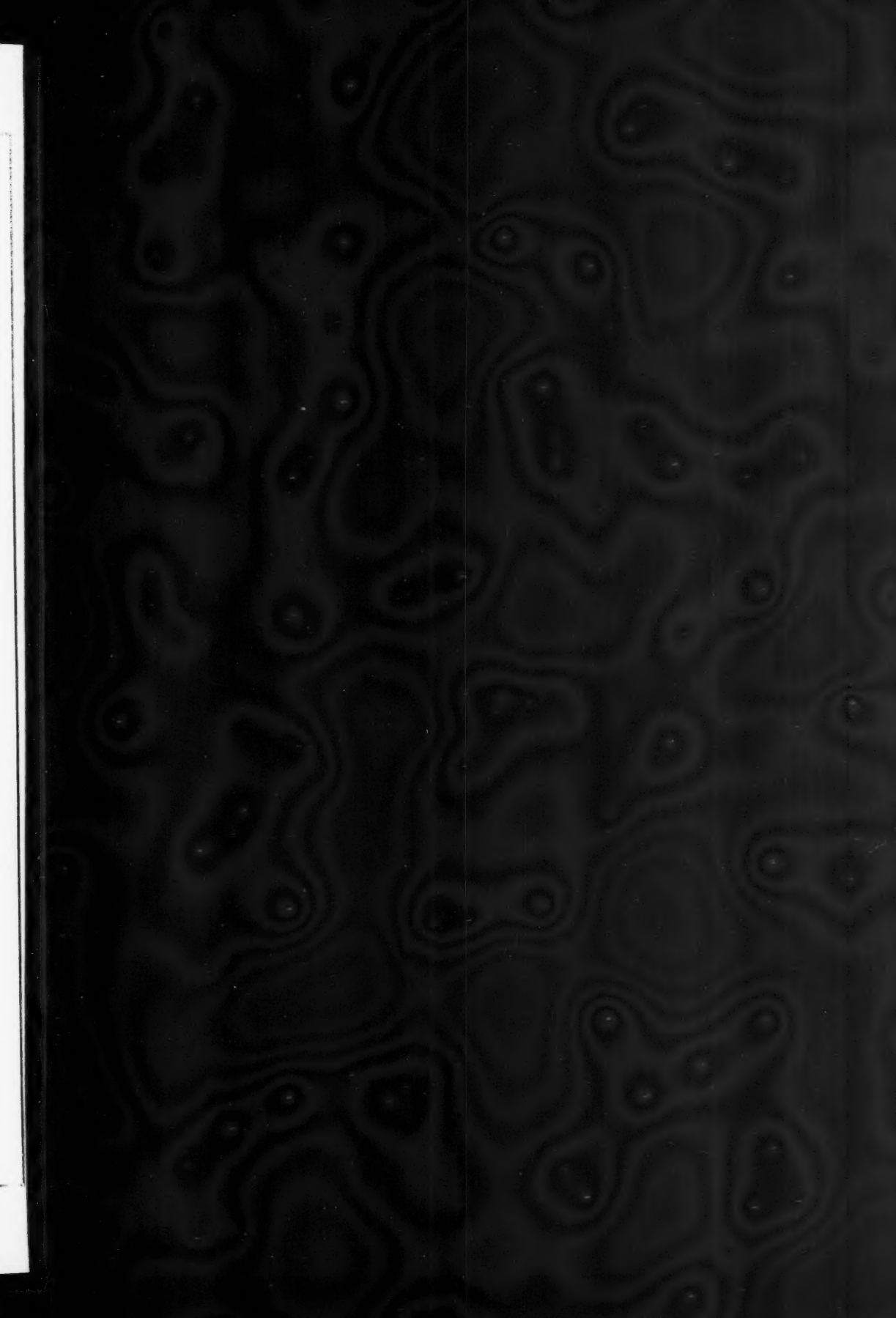
PROF. CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio

PROF. N. M. TULAIKOV
Agricultural Experiment Station, Saratov, Russia

DR. F. WEIS
Royal Agricultural and Veterinary College, Copenhagen, Denmark

PROF. S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.
Copyright, 1930, The Williams & Wilkins Company



RELATION OF NITRATES IN SOILS TO THE RESPONSE OF CROPS TO POTASH FERTILIZATION:[1] I. FACTORS CONTRIBUTING TO THE UNPRODUCTIVENESS OF "ALKALI" SOILS IN ILLINOIS

O. H. SEARS

University of Illinois Agricultural Experiment Station

Received for publication March 3, 1930

The capacity for crop production of thousands of acres of more or less unproductive soil, commonly known as "alkali," which are located in the northern half of Illinois, may be greatly increased by the application of potash salts. The need for potassium on these soils has existed for many years and was recognized previous to 1912.

On other soils, particularly in the southern third of the state, the need for potash salts appears to be developing and is usually associated with the repeated growing of sweet clover on the land.

The results reported in this paper were obtained in studies of the first group of soils, begun in 1923 to determine the reasons for crop response on these soils where potash salts were applied. As a result of many laboratory tests, greenhouse studies, and field trials, it is concluded that two factors contribute to the unproductiveness of these soils: first, a deficiency of available potassium; and second, an excessive accumulation of nitrate nitrogen.

The first of these conditions is associated with the presence of a high lime content in a large percentage of cases, although in some instances a low amount of total potassium exists.

The second factor is the result of conditions favorable for nitrate formation, particularly the presence of calcium carbonate and an abundance of readily nitrifiable organic matter.

The following observations are presented in support of the conclusion that these two factors play an important part in the responsiveness of these soils to applications of potash salts.

The "alkali" soils of Illinois, occurring in tracts which vary in size from a few square rods to many acres, are usually found in connection with swamp land that has been reclaimed by drainage and brought under cultivation. Consequently, they are usually high in organic matter and they contain an abundance of carbonates. The first one or two crops grown are ordinarily satisfactory, but subsequent yields are disappointing. Corn appears to be affected most seriously. It germinates well and makes a normal growth for a very few weeks, after which it ceases to grow, turns yellow, and finally has the appearance of being badly diseased.

[1] Published with the approval of the director. Contribution from the department of agronomy. This paper was submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of doctor of philosophy.

Small grains produce an abundant vegetation but lodge badly, and as a result a low yield of shriveled grain is produced. Sweet clover, however, makes a splendid growth.

After adequate drainage has been obtained, the capacity for crop production on these soils is greatly increased by the application of potash salts and by the use of straw, corn cobs, or manure, particularly horse manure. In fact, after such treatments, these soils frequently produce larger and better crops than the fertile land surrounding them.

A whitish deposit on the surface of these soils, when dry, is a characteristic feature which has led to the general adoption of the term "alkali" for the designation of these unproductive areas. Although it is generally recognized that the alkali differs from the black alkali of the arid regions, opinions differ as to the cause of the unproductiveness of these soils.

Unproductive soils, similar in character to those in Illinois, are known to occur in Iowa, Wisconsin, Indiana, and to some extent in other states. Although investigators in these states generally recognize the same characteristics and have improved the crop-producing capacity of these soils by the same kinds of treatment, there is considerable difference of opinion as to the cause of their unproductiveness.

King and Jeffrey (13) believed that some injurious principles exist in the soil water and that the beneficial influence of potassium-containing salts could not be in the direction of supplying needed potash for plant-food. They state that they were much surprised to find that no perceptible influence was exerted by liquid manure, whereas a very large increase was realized on the plots receiving solid manure.

Conner and Abbott (7) were of the opinion that a lack of available potassium is the factor limiting the crop yields on the Indiana soils of this character, and that the value of straw, corn cobs, and similar materials is due entirely to the potassium contained therein. They stated that "wheat and oats straw contain from seven-tenths to over one per cent of potash—practically all soluble in cold water." They concluded from this that it is obvious that no other explanation is necessary of why wheat straw is a beneficial treatment for peat soils deficient in potash. It may be added in this connection that many alkali soils not deficient in total potassium give a marked increase in yield when straw applications are made.

Bancroft (2) concluded that the presence of calcium bicarbonate is the chief soluble salt in the alkali soils of Iowa, although he agreed that the presence of other salts in addition to this compound may prove injurious. It is stated that drainage and the application of manure will remedy alkali conditions in Iowa, whereas potassium and calcareous clay have practically no influence on the reclamation of such soils. As no crop yields are reported, it is assumed that these conclusions are based upon chemical analyses alone. Analyses of the leachings of soils receiving various treatments are given, but no mention is made of the nitrate content of the soil.

Hopkins, Readhimer, and Fisher (11) were of the opinion that these soils were not improperly called "alkali," and that magnesium carbonate was the toxic substance responsible for the low crop yields. They concluded that plenty of tile, laid deep and made to work, is all that some of these alkali spots need to make them grow good corn. Subsequent investigations (18) at the Illinois Experiment Station on other kinds of soil indicate that magnesium toxicity is negligible even though a relatively high proportion of magnesium carbonate is present.

In planning the experiments which are presented here, consideration was given to the possible causes of the unfavorable soil condition or conditions resulting in low crop yields. It is obvious that the unproductiveness could be due to the absence of an essential factor, to the presence of an unfavorable influence, or to a combination of both. The treatments used in an effort to improve these soils were selected with these things in mind.

Recognizing the limitations of laboratory work, and appreciating the fact that greenhouse studies should be supplemented by field trials, the author

employed all three methods in the investigations herein reported. Furthermore, in order that any conclusions which were reached might not be too limited in their application, 10 soils from 9 counties were investigated during the progress of the work.

GREENHOUSE EXPERIMENTS

Effects of crop residues and mineral fertilizers

Preliminary results obtained by F. H. Maxfield, as a part of a student's thesis, indicated that potash salts were effective in increasing crop yields on alkali soils. Either wheat or oats straw used as a mulch was more effective, however, than the chloride or sulfate of potash, even though the straw and

TABLE 1

Weights of lettuce and wheat grown under greenhouse conditions on black sandy loam from Cass County

SOIL TREATMENT		WEIGHT OF CROPS		
Kind	Amount*	Lettuce	Wheat	
			Grain	Straw
		gm.	*gm.*	*gm.*
None	...	1.05	4.25	8.75
K_2SO_4	200	1.40	7.50	14.35
KCl	200	1.85	6.09	13.26
K_2CO_3	200	1.08	7.62	12.43
Wheat straw	5 tons mulch	2.40	8.20	13.06
Sweet clover	1 ton mulch	1.08	10.58†	17.70

* Unless otherwise stated, all soil treatment is given in terms of pounds an acre (2,000,000 pounds).

† Additional treatment of 200 pounds potassium sulfate and 500 pounds superphosphate.

potash salts contained the same amount of potassium. Sweet clover, on the other hand, was ineffective (table 1).

It appears that the use of potassium-containing salts had a beneficial effect upon the growth of lettuce and wheat. When judged by the yields of lettuce, the chloride appears to be the best of the three salts tested, and potassium carbonate the least effective. The residual effect upon the subsequent wheat crop, however, was greatest where the sulfate had been used. This difference may be accounted for by the fact that the chloride had produced the biggest crop previously. When results obtained in subsequent trials are considered, there appears to be little choice between the chloride and sulfate for use on this soil. In nearly all cases the potassium carbonate was somewhat less beneficial than either of the other two potash salts. This is probably due to its tendency to increase the alkalinity of an already too alkaline soil.

It is of interest to find that wheat straw had a more marked influence upon

the yield of lettuce than any other treatment. There are at least three possible explanations for the increased yields where the straw is applied: first, the straw served as a source of readily available potassium; second, the organic matter added in the straw reduced the toxicity of the soil by absorption of unfavorable constituents; and third, favorable changes in the microorganic population of the soil were brought about through the addition of food materials in the straw.

The investigations of many workers have proved that straw serves as a source of readily soluble potassium but it seems unlikely that the greater benefit resulting from this treatment is due solely to the potassium which it contains, since both the potassium chloride and carbonate treatments contain a larger amount of this element than the straw.

Little significance can be attached to the second point as an explanation of these observed differences in crop response because sweet clover not only furnishes potassium but also supplies organic matter; nevertheless, it had no beneficial effect upon crop yields.

The yields of both lettuce and wheat suggest that in addition to the benefit derived from the potassium contained in the straw, a biological factor is to be considered. Several investigators (6) have proved that applications of straw and other cellulosic materials lower the nitrate nitrogen content of soils. This decrease is not a permanent effect, however, for the soil returns to its normal condition after a few weeks. Since these alkali soils readily produce nitrate nitrogen, it is conceivable that in the absence of certain essential elements, such as potassium, an accumulation of nitrate nitrogen is toxic, either in itself or by lowering the resistance of the plant so that other unfavorable influences become increasingly detrimental. Under such a condition, the beneficial effect of wheat straw may be attributed to two effects; namely, the addition of available potassium and the diminution of soil nitrates. Sweet clover, on the other hand, could not be expected to exert a beneficial effect because any benefit due to soluble potassium which it contained would tend to be offset by the accumulation of nitrates induced by the sweet clover.

In the residual effect upon the wheat yields, the same tendencies are evident. The influence of potassium, whether applied as salts or in the straw, is still apparent, but the difference between the straw and potash treatments is considerably decreased. This would be expected if the effect of the straw is due partially to biological activities, for, as previously stated, the nitrate reduction is only temporary. The method of applying the straw, however, is an important factor determining the residual effect upon nitrate accumulation. When it is incorporated with the soil, as compared with the mulch method, a more pronounced immediate reduction of the nitrate nitrogen content is brought about, followed shortly by a decided nitrate accumulation. When it is used as a mulch, a less pronounced immediate effect is obtained which persists longer before excessive nitrate accumulation again occurs.

In general, the soil from Whiteside County gave results similar to those ob-

tained with the soil from Cass County (table 2). Of the three crops grown, corn is decidedly the most responsive to potash fertilization, a fact which is well recognized from general observation. The lettuce crop, however, is the only one responding to phosphate treatment, giving increases which are quite striking, particularly when used in addition to a potassium-containing salt. This observation well illustrates the possibility of error when an attempt is made to apply the results obtained from one observation to other conditions. As subsequent data will show, no evidence has been obtained indicating that corn grown on this kind of soil is responsive to phosphate treatment.

The value of straw is again strikingly demonstrated, especially where it is used in addition to the potassium salts. The treatment consisting of sweet

TABLE 2

Weights of lettuce, corn and wheat grown under greenhouse conditions on black sandy loam from Whiteside County

SOIL TREATMENT		WEIGHT OF CROPS			
Kind	Amount*	Lettuce	Corn	Wheat	
				Grain	Straw
		gm.	*gm.*	*gm.*	*gm.*
None	...	0.93	45.5	7.2	17.5
K_2SO_4	300	1.35	106.0	8.3	20.3
KCl	300	0.93	112.5	8.2	19.6
K_2CO_3	300	0.92	91.5	9.2	17.1
NaCl	300	0.85	49.0	7.5	19.7
Superphosphate	500	1.35	42.0	...	....
K_2SO_4 superphosphate	300 500	2.25	116.5	7.9	20.9
Wheat straw	2 tons	1.28	207.5†	9.1	23.8
Sweet clover	1 ton	1.04	131.0†	9.4	23.4

* Unless otherwise stated, all soil treatment is given in terms of pounds an acre (2,000,000 pounds).

† 250 pounds of K_2SO_4 and 500 pounds superphosphate in addition to previous treatment.

clover, superphosphate, and potassium sulfate cannot be considered any more effective than the corresponding treatment without the sweet clover, whereas, the straw in the same combination has had a very marked influence on the corn yields, again indicating that it owes its value in part to factors other than the potassium content. The residual effect upon the succeeding wheat crop is very small. Two conditions contribute to such a result. First, wheat appears to be less seriously influenced by the toxicity of these soils than is corn, consequently it is less responsive to the usual effective treatments. Second, the residual effect of straw treatment could not be expected to be large if its value depends upon its effect on the accumulation of nitrates in the soil, in addition, of course, to the potassium which it supplies.

Besides the effect upon crop yields, both straw and potash treatments had a marked influence upon the appearance of the plants. In the absence of soil treatment, a browning and curling of the leaf tip occurred. In some cases this condition progressed to the complete killing of many leaves. These symptoms are unlike those obtained where potassium-deficient nutrients are used for the growing of corn. The leaves of the corn in the latter case are striped but not brown and crinkled. Apparently some factor in addition to a potassium deficiency affects the leaf reaction in these soils.

Many experiments have shown that sodium chloride is effective in increasing crop yields on many potassium-deficient soils. This response has been attributed to a base-exchange phenomenon and to the direct substitution of

TABLE 3

Weights of corn grown under greenhouse conditions on deep peat soil from Cass County

SOIL TREATMENT	WEIGHT OF CORN CROP			INCREASE OVER CHECK
	1st jar*	2nd jar*	Average	
	gm.	*gm.*	*gm.*	*per cent*
None	44.8	55.0	49.9	...
2.5-ton straw mulch	116.5	115.3	115.9	132.2
5.0-ton straw mulch	151.1	153.8	152.5	205.6
Ashes from 2.5 tons straw	89.8	75.3	82.6	65.5
Ashes from 5.0 tons straw	91.0	111.3	101.2	102.8
1-ton sweet clover mulch	94.3	97.3	95.8	92.0
3-ton sweet clover mulch	130.3	132.3	131.3	163.1
Ashes from 1 ton sweet clover	90.3	86.2	88.3	77.0
Ashes from 3 tons sweet clover	113.0	132.3	122.7	145.9
200 pounds potassium chloride	112.7	113.0	112.9	126.3
5.0-ton straw mulch plus 200 pounds potassium chloride	163.0	161.0	162.0	224.6
Ashes from 5.0 tons straw plus 200 pounds potassium chloride	143.3	140.7	142.0	184.6

* Average of three successive crops upon the same jar.

potassium by sodium in the nutrition of the plant. In this experiment, however, sodium chloride failed to affect any of the crop yields materially.

Comparison of straw and sweet clover with their ashes

The two previous experiments indicated that the value of straw for the improvement of these alkali soils was not confined to the potassium it contained. If, in addition to supplying this element, a beneficial influence was exerted through a lowered nitrate nitrogen content as a result of microorganic activity, it follows that unburned straw should have a more marked effect upon crop yields than would its ashes. On the other hand, sweet clover would not be expected to be more effective than its ashes since it would supply only one factor—potassium—and would not lower the amount of soil nitrates, but rather tend toward increasing them.

Table 3 gives the results of an experiment designed to test this hypothesis.

These results were obtained on a soil located one-fourth mile from the Cass County soil used in the previous experiment. It is somewhat higher in organic matter, but, as can be seen from a comparison of the results, responds to treatment in a manner similar to that of the other soil.

It may be seen that a mulch consisting of 2.5 tons of straw to the acre was less effective in increasing corn yields than was a 5-ton application, and that a straw mulch was twice as effective as the ashes from the corresponding amount of straw.

In the case of sweet clover, however, there was little difference between the mulch and the ashes. On a percentage increase basis there appeared to be an advantage in favor of the unburned sweet clover, but an inspection of the duplicates shows that the difference was within the range of experimental error. It appears, therefore, that the wheat straw supplies a factor favorably influencing the growth of corn and which may be lost by burning, whereas the sweet clover is lacking in this factor. Furthermore, 2.5 tons of straw supplied in the form of a mulch results in a larger increased corn yield than an amount of potassium chloride supplying twice as much potassium. The results are in agreement with those reported in table 2 for another soil.

Effect of growing sweet clover upon subsequent yields

Sweet clover makes an excellent growth on alkali soils in Illinois. It would be reasonable to assume that if a potassium deficiency were the sole factor limiting yields on these soils, the growing and plowing under of a sweet clover crop should increase crop yields, the beneficial effect being obtained by the release through decomposition of the potassium contained in the sweet clover plants. Field observations on a Cass County farm failed to justify such an assumption, however, for the poorest corn in the field was found on the area where the largest amount of sweet clover was plowed down. This condition might have been attributed to a moisture effect, were it not for the fact that splendid corn was grown under the same conditions where potassium chloride was applied. It seemed desirable, therefore, to determine under controlled greenhouse conditions the extent to which sweet clover would restore the productive power of these soils. Consequently, an experiment was begun in which biennial white blossom sweet clover was grown in some jars while other jars containing the same kind of soil were allowed to remain fallow although kept at the same moisture content. When the sweet clover had attained a height of about 18 inches, tops and roots were returned in some cases to the soil in which they grew, whereas in other cases they were removed and placed in fallow soil. All of the jars were planted to corn, which produced the yields reported in table 4.

It cannot be said that the growing of sweet clover on this soil had a marked influence on its productive capacity, since the average yield of jars 11 and 12 with sweet clover is little above the average of the checks, jar 12 being but 0.9

gm. heavier than jar 13. For a similar comparison, jars 3, 4, 9, 10 may be considered. When the variation between duplicates is considered, there is little evidence to indicate that the sweet clover, in addition to the potassium chloride, has had any pronounced effect. It is evident, however, that the sweet clover crop has taken something of value, apparently potassium, to the corn crop from jars 5 and 6 and added it to jars 7 and 8. In this connection, it is of interest to note that the average decrease in yield on the soil from which the sweet clover has been removed is 52 gm. and that the gain where the sweet clover tops were added is 40 gm. The results from this single experiment are too meager to warrant a statement to the effect that sweet clover will not improve this kind of soil. The data are suggestive, however, and indicate that on this one soil any benefit which is derived from an increased availability of potassium brought about by the growing and returning of the sweet clover may be nullified by the increased nitrate nitrogen which accumulates as a result of the rapid decay of the sweet clover.

TABLE 4

Weights of corn grown under greenhouse conditions on black sandy loam from Cass County, as influenced by a sweet clover green manure crop

JAR NO.	SOIL TREATMENT		CORN WEIGHTS FOLLOWING SECOND TREATMENT	
	First	Second	Average	Individual
			gm.	*gm.*
1	Fallow	None	133.0	130.7
2				130.8
13				137.4
3	Fallow	KCl—150 pounds an acre	189.1	178.7
4				199.5
5	Sweet clover	Sweet clover removed—tops and roots	81.0	80.0
6				82.0
7	Fallow	Sweet clover tops from 5 and 6 added	173.0	173.0
8				172.9
9	Sweet clover	Sweet clover returned—KCl —150 pounds an acre	188.8	191.5
10				186.1
11	Sweet clover	Sweet clover returned	141.6	144.7
12				138.5

Relation of temperature and moisture to crop yields and nitrate accumulation

It is a common observation that the yield of crops produced on these alkali soils varies more widely from season to season than on most soils. The most

productive areas appear to lie either in the most poorly drained part of the field or along the tile drains, whereas the least productive areas are intermediate in position. These better yields in the favorable seasons and on the more productive areas may be due to a condition favorable for maximum crop utilization of potassium or to a condition that limits the accumulation of a toxic substance, such as an excess of nitrates. In order to determine which of these conditions obtains, the response of an alkali soil to potash treatment was studied at different moisture and temperature conditions in the greenhouse. During the season of 1927 the field from which the soil was taken produced 5.75 bushels of corn to the acre without treatment and 60 bushels an acre where muriate of potash was hill-dropped at the rate of 75 pounds an acre.

After reaching the greenhouse, the soil was leached with distilled water in order to remove most of the soluble salts, particularly nitrates, dried to a

TABLE 5

Influence of moisture and temperature upon nitrate content of a brown sandy loam from McHenry County

INCUBATION PERIOD	NITRATES IN DISPLACED SOIL S LUTION					
	Soil moisture content					
	21 per cent			32 per cent		
	Soil temperature					
	16°C.	23°C.	30°C.	16°C.	23°C.	30°C.
days	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
21	448	533	664	330	425	512
49	535	518	971	510	652	861

moisture content of 21 per cent, then sieved, and thoroughly mixed. Asphalt-painted galvanized containers were filled with equal weights of the soil and then placed in constant-temperature tanks held at 16, 23, and 30° C. respectively. At this time the soil contained 60 p.p.m. of nitrates (NO_3) in the displaced soil solution. The soil in half of the containers at each temperature was held at a moisture content of 21 per cent, while in the other half it was maintained at 32 per cent. The soil was kept under these several moisture and temperature conditions for three weeks, after which it was planted to corn. One series under these same conditions was kept fallow for chemical studies, in order that the trend of nitrate accumulation might be followed. The nitrate content of the fallow soil at the time of planting and harvesting of the corn is shown in table 5.

It is clear that the speed of nitrate accumulation has been greatest in the soils which were kept at a low moisture and at the highest temperature, whereas the least accumulation occurred where the moisture content was high and the temperature low.

The response of the corn crop under these moisture and temperature conditions to an application of potassium chloride at the rate of 450 pounds an acre is recorded in table 6.

It is apparent that moisture and temperature influenced the responsiveness of these soils to potash applications. It is of interest to find that the combination of moisture and temperature which resulted in the lowest nitrate content both at the time of planting and harvesting is the one which gave the greatest increase in corn yield for potash fertilization, and that the soil having the highest nitrate content at planting and harvest times gave the smallest response to the application of potash salts. It may be concluded that the conditions which affect the rate of nitrate accumulation also influences the seasonal response of crops on these soils. Therefore, comparatively poor corn yields may be expected in seasons which favor the accumulation of nitrates.

TABLE 6

Influence of potassium chloride upon the weight of corn grown on brown sandy loam from McHenry County, at different moisture and temperature conditions

SOIL TEMPERATURE	WEIGHT OF CORN				DIXON SOIL CHECK
	21 per cent moisture		32 per cent moisture		
	None	KCl	None	KCl	
°C.	gms.	gms.	gms.	gms.	
16	0.54	0.89	0.55	1.13	0.92
23	0.77	1.17	0.78	1.26	1.15
30	1.14	1.41	1.08	1.38	1.85

TABLE 7

Corn yields on black sandy loam in Cass County

NO. PLOTS IN AVERAGE	SOIL TREATMENT		CORN YIELDS	INCREASE OVER CHECK
	Kind	Rate per acre		
		lbs.	bu.	per cent
6	None	.....	28.5	....
4	Straw	6,000	43.9	54.0
3	KCl	150	69.1	142.4
3	KCl	200	66.9	134.7
4	KCl + Straw	150 to 200 + 6,000	69.0	142.1

FIELD EXPERIMENTS

Cass County experiment

In order to be of the greatest value, greenhouse trials should be supplemented by field experiments. For that reason, field studies were conducted on four

soils in four counties of the state. It seemed desirable in the beginning to study in the field a soil that had been used in the greenhouse. Consequently, the first field experiment was conducted on the black sandy loam soil in Cass County from which the greenhouse soil had previously been obtained. A summary of the results is given in table 7.

Farm practice, particularly cultivation, made it impossible to use the straw as a mulch, and hence it was necessary to plow it under. The smaller response in the field is attributed to this difference in method of application. The results are comparable, however, to the greenhouse results reported in table 2, where the straw was incorporated in the soil. The difference in response brought about by the method of handling straw may be understood when consideration is given to the fact that two factors are responsible for the increased yields. When enough straw to give an adequate supply of potassium for crop needs is plowed under, the soil microorganisms are encouraged to such an extent that they compete with the corn crop for nitrates. This is shown by

TABLE 8

Alfalfa yields on black mixed loam in Winnebago County

LOT NO.	SOIL TREATMENT		YIELD PER ACRE	INCREASE OVER CHECK	
	Kind	Rate per acre			
		lbs.	*lbs.*	*lbs.*	*per cent*
1	Muriate of potash	160	1,114	536	92.7
2	Straw	4,000	1,213	635	109.9
3	Straw Muriate of potash	4,000 160	1,241	663	114.7
4	None	...	578	...	...
5	Muriate of potash	200	1,114	536	92.7

the nitrate nitrogen content of the soil on July 15, at which time the soil without straw contained 201 pounds an acre in the surface soil and 211 pounds in the subsurface, whereas the land with straw contained no determinable amount in the surface and only 22.5 pounds to the acre of nitrate nitrogen in the subsurface. When applied as a mulch, however, the amount of organic matter made available in proportion to the potassium leached into the soil is relatively smaller. Consequently a favorable effect is produced.

The muriate of potash broadcast at rates of 150 and 200 pounds an acre immediately after the corn was planted gave equally good results at both rates.

Winnebago County experiment

In spite of the fact that alfalfa makes a better growth than corn on untreated alkali soil, definite increases in the yields of alfalfa hay have been obtained in Winnebago County from the applications of the same kinds of fertilizer materials which have proved effective on alkali soils of the state. The yields of alfalfa obtained from one cutting in 1926 are given in table 8.

The value of straw and potassium-containing salts for the improvement of alkali soil is again demonstrated by this field experiment. Although less than one-half as much potassium is applied in the straw as is added in the form of potash salts, the gain is apparently somewhat greater.

McHenry County experiment

A field experiment conducted in 1927 on a brown sandy loam on sand in McHenry County gave results which are similar to those obtained on the two fields previously discussed. A summary of the results is given in table 9.

It is obvious that all treatments except the superphosphate have had a favorable influence upon the yield. The large difference in favor of the hill-dropped muriate of potash at the low rate used was somewhat unexpected. Laboratory studies, which are reported later, indicate that this difference in effectiveness is due to the great capacity for the absorption of salts exhibited by this soil.

TABLE 9

Corn yields on brown sandy loam on sand in McHenry County

NO. OF PLOTS	SOIL TREATMENT		CORN YIELDS PER ACRE	INCREASE PER ACRE
	Kind	Rate per acre		
		lbs.	*bu.*	*bu.*
6	None	....	5.75	....
1	KCl*	75	60.00	54.25
2	Straw	6,000	24.80	19.05
2	Superphosphate	320	2.50	−3.25
3	KCl†	160	22.30	16.55
2	Cow manure	16,000	40.00	34.25
2	Horse manure	16,000	68.50	62.75

* Hill-dropped.

† Broadcast.

In order to apply the fertilizer broadcast at the same rate per unit area of soil as it is applied to the small area surrounding the hill by hill-dropping, several thousand pounds an acre would be required. Consequently, where the fertilizer is hill-dropped, available potassium remains for the nutrition of the corn plant after the absorptive capacity of the soil is satisfied. This condition is not attained with the broadcast distribution and as a result much better yields result from hill-dropping 75 pounds of potash salts than are obtained by broadcasting the material at the rate of 160 pounds an acre.

For the reasons mentioned, the straw treatment has been less effective than the hill-dropped potash salts and practically as effective as the broadcast fertilizer. Unfortunately, weather conditions prevented the use of straw as a mulch, as had originally been planned. Reasons have already been presented for the belief that such a method would have been more effective than plowing under the straw.

The importance of the physiological balance in soils is illustrated by a comparison of the yields from horse and cow manures. Both manures supplied available potassium but only the horse manure had the tendency to lower nitrate accumulation. This fact is well shown by Allison (1) who found that the unfavorable effect of manure on soils containing meager amounts of available nitrogen was due to the stimulation of biological activities with the resulting nitrate assimilation. In such soils where a lack of available nitrogen was a limiting factor, the cow manure was more than 100 per cent better than the horse manure for the first crop. For the same reason, the horse manure is 70 per cent more effective on soil in McHenry County where an excess of nitrates is a limiting factor.

The pronounced effect on crop growth resulting from the application of the horse manure is shown in plate 1.

TABLE 10

Composition of four types of snail shells found in Illinois alkali soils

SAMPLE		INSOLUBLE MATTER	CALCIUM	CALCIUM CARBONATE		MAGNESIUM CARBONATE BY DIFFERENCE
No.	Name*			Calculated from total Ca	Equivalent by titration	
		per cent	*per cent*	*per cent*	*per cent*	*per cent*
1	*Polygyra monodon* (Rackett)	1.92	36.4	91.0	96.8	4.87
2	*Helisoma trivalvis* (Say)	0.99	37.6	94.0	97.4	2.86
3	*Physa gyrina* (Say)	1.41	37.2	93.0	97.5	3.78
4	*Stagnicola umbrosa* (Say)	0.68	36.5	91.25	92.9	1.39

* Identified by Prof. F. C. Baker.

LABORATORY INVESTIGATIONS

Both greenhouse and field experiments showed the importance of two factors in limiting the yield of crops on alkali soils. These points have been stressed in the discussion of the tests made and even though the evidence seemed conclusive, it appeared desirable to establish the correctness or fallacy of these conclusions by laboratory investigations.

Composition of snail shells

Previous investigators had attributed the toxicity of these soils to the presence of magnesium carbonate, although they state that considerable amounts of calcium carbonate accompany this constituent. Since shells are so common in these soils, a determination of the calcium and magnesium content of shells which appear to be typical seemed worth while. Table 10 gives the comparison of four representative lots.

In the light of the more recent information upon the subject of the calcium/magnesium ratio in its relation to crop production, these data lend little support to the belief that magnesium toxicity is a factor contributing to the unpro-

ductiveness of these soils, especially if the shells furnish any considerable part of the total amount of these elements contained in the soil.

Composition of three alkali soils

Further data bearing on this relationship are given in table 11, which shows the percentage of nitrogen, calcium, magnesium, and potassium in three alkali soils.

The ratio of calcium to magnesium varies from 2.7:1 to 15:1, ratios which contain considerably more calcium than the proponents of the calcium/magnesium ratio theory considered necessary to prevent the toxicity of magnesium carbonate.

These analytical data are also in accord with the statement made in the introduction that these soils are high in nitrogen and usually alkaline in reaction. The deep peat soil from Cass County is an exception to the latter rule, but it is unusually high in nitrogen and somewhat low in potassium. Consequently, it gives striking increases in crop yield when either straw or potash

TABLE 11

Chemical composition of three Illinois alkali soils

COUNTY	NITROGEN	CALCIUM	MAGNESIUM	POTASSIUM	REACTION
	per cent	*per cent*	*per cent*	*per cent*	*pH*
McHenry	0.398	0.85	0.320	0.774	7.30
Cass I	1.790	1.45	0.301	0.755	5.45
Cass II	0.465	5.45	0.346	0.839	8.35

salts are applied (table 3). None of these soils can be said to be actually deficient in total potassium, however, for they contain, on the average, one-half as much of this element as the usual productive corn-belt soils. Apparently their responsiveness to potash treatment is due to a condition causing a low availability, or to a factor increasing the need of available potassium, or to both. Analyses of other soils of a similar character have given results much like those just discussed.

Availability of soil potassium

McIntire (14), Plummer (15), Ehrenberg (8), and others have called attention to the fact that the availability of soil potassium is lowered by the presence of calcium carbonate. Ehrenberg has gone so far as to formulate a lime-potash law and warns against the application of large quantities of limestone. He states that any unfavorable condition resulting from liming may be counteracted by side-dressings of potash salts. Since the alkali soils in Illinois are well supplied with carbonates, it appeared quite probable that the low crop yields resulted at least in part from a lack of available potassium. Conse-

quently, tests were made to determine whether this was the case. Of the methods designed for the estimation of availability, two were used; namely, determinations of the potassium concentration in the displaced soil solution (4), and the determination of potassium replaced by a neutral salt. These two methods, which are assumed to show immediate and potential availability, should give results which are indicative of the condition of the soil potash so far as its usefulness for crop growth is concerned.

Soils ordinarily contain from 20 to 100 p.p.m. of potassium in the displaced solution. Burd (3) found that three sandy loam soils which he studied contained 26, 49, and 78 p.p.m. respectively. In contrast to this, the displaced solution from the McHenry County soil contained less than 1 p.p.m. of potassium. It is apparent, therefore, that but little potassium exists in this soil in a readily soluble form. Similar results were obtained with other alkali soils and in no case were there more than 8 p.p.m. of potassium found in the displaced solution, and that in one of the more productive of the alkali soils.

Evidence of low availability was found also in the small quantity of replaceable potassium in the McHenry County soil. Only 46 p.p.m. was found in this soil, whereas Vandecaveye (17) reports the presence of 182 p.p.m. of replaceable potassium in untreated Carrington loam in Iowa. Unpublished results from the Ohio station indicate a somewhat similar amount of replaceable potassium in productive soils in that state. Since this McHenry County soil is very low in both water-soluble and replaceable potassium, it is not surprising that it is so highly responsive to fertilizers containing this essential element.

Absorption of potash salts

Although the preceding observations explain the responsiveness of these soils to potash fertilization, they do not furnish the reason for the greater effectiveness of hill-dropped salts, particularly since the acre-rate of application was less than one-half as high as in the broadcast method. There yet remains the possibility that the same condition contributing to the low availability of the native soil potassium may also render applied potash salts unavailable.

In order to determine whether this situation obtained and to ascertain what factors were involved if it did exist, five 4-kilo samples of the soil were used in an experiment in which four different amounts of potassium chloride were added to four of the samples, the fifth sample being retained as a check. After thorough mixing, the soils were maintained at approximately 60 per cent of their water-holding capacity. Three samples of each of the five soils were then used for the following determinations:

Sample 1 (a) Water-soluble potassium not fixed by the soil.
(b) Water-soluble calcium replaced by the potassium chloride.
Sample 2 (a) Potassium exchangeable with 0.1 *N* $BaCl_2$.
Sample 3 (a) Potassium content of the soil solution.

The first sample remained for one week in the moist condition and then was leached with distilled water until the percolate was free from soluble calcium. The potassium and calcium contents of the leachings were then determined and the amount of potassium converted into a non-leachable form was ascertained by difference.

Obviously this soil has a great capacity for the absorption of salts because less than 3 per cent of the potassium applied as the chloride remained in a soluble form, even when the rate of application was as high as 600 pounds an acre (table 12). Apparently the potash salt is so completely absorbed when broadcast at the rate of 160 pounds an acre that little remains in a soluble form for the nutrition of the plant.

These data also explain another observed phenomenon, namely, the negligible residual effect of potash salts on these soils, which necessitates repeated applications. This fact has been explained ordinarily by the statement that any residual fertilizer material is largely leached out between cropping seasons.

TABLE 12

Absorption of potassium chloride by brown sandy loam from McHenry County

TREATMENT NO.	RATE OF APPLICATION		POTASSIUM LEACHED		AMOUNT OF ADDED K	
	K per kgm.	KCl per acre	Total	Added	Recovered	Absorbed
	gm.	*lbs.*	*gm.*	*gm.*	*per cent*	*per cent*
0	.....	.....	0.004	.....	....	.....
1	0.0394	150	0.0051	0.0011	2.79	97.21
2	0.0788	300	0.0051	0.0011	1.40	98.60
3	0.1576	600	0.0084	0.0044	2.79	97.21
4	0.3152	1,200	0.0296	0.0256	8.12	91.88

This appeared reasonable since many of the soils are sandy loams. It now appears more likely that repeated applications are necessary on account of fixation rather than leaching.

Whenever a soluble salt is added to a soil, an equilibrium is established between the added ions and the soil constituents. Recent investigations by Hissink (10), Gedroiz (9), Kelly (12), and other workers have shown that the colloidal portions of the soil have an important rôle in this reaction. According to their findings, the potassium ion would be expected to replace other positive ions in the colloidal complex and could in turn be replaced by some other ions, and, in this replaceable condition, the potassium is assumed to be potentially available.

Since both field and laboratory investigations gave evidence that added potash salts are changed into unavailable forms, it seemed desirable to determine what proportion had been absorbed as a part of the colloidal complex. Sample 2 was used for this purpose, $BaCl_2$ being used as the displacing agent (5). The amounts of water-souble calcium released by the potassium chloride

applications as determined in sample 1 are compared with the exchangeable potassium found from an analysis of sample 2.

These data indicate that from 50 to 70 per cent of the potossium applied as chloride has been used in releasing calcium ions, the amount depending upon the concentration of chloride used, and that with the exception of the largest application, not only a large total amount of calcium was released with the increasing rate of application but also an amount greater in proportion to the potassium added. On the other hand, excepting the highest rate of application, a progressively smaller percentage of potassium is absorbed in a

TABLE 13

Effect of potassium chloride additions upon water-soluble calcium and replaceable potassium in brown sandy loam from McHenry County

TREATMENT NO.	K FIXED BY SOIL*	WATER-SOLUBLE Ca REPLACED BY KCl	ABSORBED K UTILIZED IN Ca REPLACEMENT	K REPLACEABLE BY 0.1*N* $BaCl_2$	
				Absorbed	Total
	gm.	*gm.*	*per cent*	*per cent*	*p.p.m.*
0	.....	.....	....	....	46.0
1	0.0383	0.0102	51.9	74.0	74.4
2	0.0777	0.0252	63.3	48.0	82.4
3	0.1532	0.0566	72.0	27.4	88.0
4	0.2896	0.0980	66.0	29.3	130.8

* Calculated from columns II and VII of table 12.

TABLE 14

Analyses of displaced solution from brown sandy loam previously treated with potassium chloride at various rates

TREATMENT NO.	K ADDED PER ACRE	K CONTENT OF DISPLACED SOLUTION
	lbs.	*p.p.m.*
0	0	0.16
1	150	0.20
2	300	0.16
3	600	0.72
4	1,200	3.40

replaceable form as the concentration of applied salts increases. Unlike soils which are neutral or acidic in reaction, here is a condition wherein only small portions of adsorbed salts can be recovered by leaching with other neutral salts.

Composition of displaced soil solution

A third portion of each of the soils receiving the potassium chloride application was used in determining the potassium content of the displaced solution. They were allowed to stand at approximately 60 per cent of their water-holding capacity for 21 days in order to establish a condition of equilibrium. A dis-

placement with water was then made and the solution analyzed with the following results.

A comparison of tables 13 and 14 shows that a close relationship exists between the replaceable potassium and the amount of this element in the displaced solution. It is significant that this soil, on which corn showed comparatively little response to an application of 160 pounds of muriate of potash under field conditions, shows little change in the soil solution with small applications of potassium salts, and that even when applied at a high rate, the amount in the soil solution is much less than most soils contain.

In addition to the low available potassium content, the importance of a high soil nitrate-nitrogen content in limiting crop yields has been mentioned. Table 5 shows that this soil not only produces nitrates, but that they are formed rapidly, going from 60 p. p. m. to 971 p. p. m. in a period of 49 days. In fact, a large part of the soluble salts which appear on the surface of the soil as a whitish deposit is composed of calcium nitrate and sulfate. The nitrate gives to the soil a characteristic brownish appearance, whereas the sulfate is

TABLE 15

Composition of displaced soil solution of three alkali soils

COUNTY	MOISTURE CONTENT	ION CONCENTRATION OF DISPLACED SOLUTION						
		Ca	SO_4	NO_3	Mg	K	PO_4	Al
	per cent	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
McHenry	22.0	160.0	48.0	430.0	48.0	0.10	0.04	Trace
McLean	31.9	390.0	135.0	910.0	19.0	8.00	0.10	Trace
Rock Island	22.8	578.0	1,040.0	1,532.0	....	0	0.03	Trace

distinctly white. Analyses showed that the displaced solution from two of these soils contained 45 and 53 per cent respectively of the total solids in the form of calcium nitrate, the remainder being composed of a combination of calcium, sulfate, magnesium, and sodium ions with traces of other elements. The distribution of the more important ions in three other typical alkali soils is given in table 15.

It is apparent from these results, which have been confirmed by numerous other analyses, that these soils furnish a displaced solution which is low in potassium and phosphate and correspondingly high in calcium, nitrate, and sulfate ions. It should be stated that the first two ions are found in fairly constant amounts, whereas the three latter vary from time to time, depending upon their removal by leaching, utilization by higher or lower plants, and accumulation as a result of nitrification. The latter statement is based upon the fact that sulfate and calcium solubility is greatly affected by the process of nitrate formation.

GENERAL DISCUSSION OF RESULTS

The laboratory, greenhouse, and field results indicate that the unproductiveness of the alkali soils of Illinois is not due to a single condition but to a combination of factors. Chief among these is a lack of available potassium and a concentration of nitrate nitrogen which is harmful. The toxicity of the nitrate nitrogen is not due solely to the presence of the nitrates, but results from an accumulation of these salts in the absence of available potassium. This assumes that a favorable physiological balance is desirable, particularly with reference to potassium and nitrate nitrogen.

The data presented show that these soils in general are not markedly deficient in total potassium but that they are lacking in an available supply of this element, as judged by the potassium content of the displaced soil solution, by replaceable potassium, by the effect of applied potash salts upon the crop yields, and by the absorption of applied potassium in non-replaceable combination. The investigations of several workers have shown that the availability of this element is lowered by liming, consequently it appears highly probable that the deficiency of usuable potassium is the result of the high carbonate content. The fact that the crop yields on an acid peaty soil were unfavorably influenced by a 50-ton application of high calcium limestone further substantiates this idea. Evidence that nitrate accumulations are also to be considered as an unfavorable factor is found in the following observations.:

Applications of straw as a mulch have a much more pronounced benefit upon crop yields than an amount of potash salts containing an equivalent quantity of the element potassium.

The immediate effect of straw is beneficial, whereas sweet clover has little favorable influence, in spite of the fact that it contains potassium. That sweet clover has a positive influence upon nitrate accumulation whereas straw has a negative effect, has been well established by other investigators.

Straw ashes are less beneficial than the unburned straw when it is used as a mulch, whereas the sweet clover ashes are fully as effective as the unburned sweet clover. Such a result is in accord with the idea that the difference between these two materials for improvement of alkali soils depends upon their effect upon nitrate accumulation. Consequently, it is doubtful whether the use of sweet clover can be depended upon for the immediate improvement of these soils, except perhaps where they possess a clay subsoil from which potassium may be extracted in relatively large amounts. Its effectiveness would be limited by the fact that nitrate accumulation induced by the decaying sweet clover would offset to a large extent any favorable influence that might be exerted by the potassium rendered available through the growing and subsequent death of the plant.

Since sweet clover makes a rank growth on many of the alkali soils without potash application, it is apparent that the potassium contained in the soil is not completely unavailable; in fact, Russell (16) states "that clovers have less capacity for absorbing potassium from the soil solution than the grasses." Inasmuch as this crop uses relatively large quantities of nitrogen in proportion to the potassium requirement, it seems probable that these soils would furnish a more favorable environment for this than for other crops requiring more potassium and less nitrogen.

Horse manure is much more valuable than cow manure for improving this kind of land. Other investigators have found that horse manure lowers nitrate accumulations, whereas cow manure tends to increase them. Consequently, the latter is superior for soils having a deficiency of

available nitrogen, particularly for the first crop. It is for the same reason that the horse manure is more effective on these soils than cow manure.

These soils contain large amounts of calcium nitrate, which is easily removed by leaching but which quickly reappears as a result of nitrification.

One Bureau County soil produced more than 600 p.p.m. of nitrate nitrogen as measured in the displaced solution in a period of seven days. Obviously, adequate drainage will not bring about the permanent removal of the soluble salts except as it encourages more rapid decay of the easily oxidizable organic matter. Good drainage is desirable, however, for other reasons and when accompanied by the use of non-nitrogenous organic matter, and the application of potash salts is indispensable for permanent improvement of these lands.

SUMMARY

The unproductivity of numerous areas of land in the northern half of Illinois is caused, not by a single condition, but is the resultant of two factors; namely, low availability of potassium and an excessive amount of nitrate nitrogen.

The low availability of potassium on most of these soils is due to an alkaline reaction rather than to a marked deficiency of this element.

The value of straw for improving the crop-producing capacity of the soils is attributed in part to the potassium which it contains. In addition, the crop is favored by a lowering of the nitrate nitrogen content of the soil resulting from the straw application. This explains the greater efficiency of unburned straw compared to its ashes in increasing yields.

For the same reason, horse manure is more valuable than cow manure on these soils, whereas the opposite condition obtains on soils in which a deficiency of available nitrogen is a limiting factor.

A favorable physiological balance in the soil is desirable, particularly with respect to potassium and nitrate nitrogen.

REFERENCES

(1) Allison, F. E. 1927 Nitrate assimilation by soil microorganisms in relation to available energy supply. *Soil Sci.* 24: 79–94.

(2) Bancroft, R. L. 1918 The "alkali" soils of Iowa. Iowa Agr. Exp. Sta. Bul. 177.

(3) Burd, J. S. 1925 Relation of biological processes to cation concentrations in soils. *Soil Sci.* 20: 280–283.

(4) Burd, J. S., and Martin, J. C. 1923 Water displacement of soils and the soil solution. *Jour. Agr. Sci.* 13: 265–295.

(5) Burgess, P. S., and Breazeale, J. F. 1926 Methods for determining the replaceable bases of soils, either in the presence or absence of alkali salts. Ariz. Agr. Exp. Sta. Tech. Bul. 9.

(6) Collison, R. S., and Conn, H. J. 1925. The effect of straw on plant growth. N. Y. (Geneva) Agr. Exp. Sta. Tech. Bul. 114.

(7) Conner, S. D., and Abbott, J. B. 1912 Unproductive black soils. Purdue Agr. Exp. Sta. Bul. 157.

(8) Ehrenberg, P. 1919 Das Kalk-Kali Gesetz. *Landw. Jahrb.* 54: 1–159.

(9) Gedroiz, K. K. 1912–25 Series of papers translated by S. A. Waksman, 1923, vols. 1 and 2.

(10) HISSINK, D. J. 1925 Base exchange in soils. *Trans. Faraday Soc.* 20: 551–566.
(11) HOPKINS, C. G., READHIMER, J. E., AND FISHER, O. S. 1912 Peaty swamp lands; sand and "alkali" soils. Ill. Agr. Exp. Sta. Bul. 157.
(12) KELLEY, W. P., AND BROWN, S. M. 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.
(13) KING, F. H., AND JEFFERY, J. A. 1900 The character and treatment of swamp or humus soil. Wis. Agr. Exp. Sta. Bul. 80.
(14) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 A 5-year lysimeter study of the supposed liberation of soil potassium by calcic and magnesic additions. *Soil Sci.* 16: 217–223.
(15) PLUMMER, J. K. 1918 Availablity of potash in some common soil-forming minerals. Effect of lime upon potash absorption by different crops. *Jour. Agr. Res.* 14: 297–315.
(16) RUSSELL, E. J. 1927 Soil Conditions and Plant Growth. London.
(17) VANDECAVEYE, S. C. 1924 Replacement of soil potassium. *Soil Sci.* 17: 91–96.
(18) WYATT, F. A. 1916 Influence of calcium and magnesium compounds on plant growth. *Jour. Agr. Res.* 6: 589–619.

PLATE 1

EFFECT OF HORSE MANURE ON CORN CROP GROWN ON A BROWN SANDY LOAM ON SAND IN McHENRY COUNTY

FIG. 1. Horse manure plowed under at rate of 8 tons an acre previous to planting corn.
FIG. 2. No soil treatment.

FIG. 1

FIG. 2

THE STATE OF UNSATURATION OF THE SOIL IN RELATION TO ITS FIELD BEHAVIOR AND LIME REQUIREMENT

P. E. TURNER

The Imperial College of Tropical Agriculture, Trinidad, B. W. I.

Received for publication March 14, 1930

That a portion of the metallic elements and of the hydrogen present in soils is capable, under suitable circumstances, of passing into the ionic state and entering into double decomposition with the cations of salts has been established by many investigators. The ions, called for this reason "exchangeable ions," found in appreciable quantities in the vast majority of agricultural soils are six; namely, hydrogen, sodium, potassium, ammonium, magnesium, and calcium. Two others, iron and aluminium, are frequently, but not invariably, present. The extent to which ionization can proceed appears limited to a fairly well-defined value, largely dependent on the soil content of inorganic and organic colloidal material. This value, denoted by the term "saturation capacity," varies from soil to soil, but is independent of the proportions in which the various ions occur (8).

The investigations of Gedroiz, Hissink, and others have demonstrated that the numerical relationship which exists between the ions is nevertheless of extreme importance, in that upon it the physico-chemical properties and the field behavior of the soil largely depend. Each positive ion, when associated with the colloidal complex of the soil, appears to form a compound with unique characteristics, and if present in preponderating amounts, impresses its ndividual peculiarities on the soil as a whole. Sodium and hydrogen ions, for example, accentuate the hydrophilic nature of the colloidal material, thereby emphasising its tendency to exist in a dispersed, deflocculated condition when moist and to compact to a cemented mass when dry (5, 7, 17, 30). Ammonium, potassium, and magnesium ions appear to exert a similar but decreasingly marked effect (7, 30). Calcium, iron, and aluminium ions render the colloidal material, by comparison, hydrophobic, and modify its properties to more desirable proportions (7, 17, 30).

The data which have been accumulated show that under normal circumstances in humid regions the soil content of exchangeable sodium, potassium, magnesium, iron, and aluminium is, as a rule, so small that the ions can exert but a minor influence on soil behavior. The investigations of McLean and Robinson (25) demonstrate that ammonium ions rarely occur in sufficient quantity to possess an appreciable effect. There is abundant evidence that exchangeable calcium usually exists in significant amounts, which may exceed 1 per cent of the total weight of the air-dry soil. Information with regard to the hydrogen ion is less definite and somewhat contradictory. Gedroiz found that although many "base unsaturated" Russian soils contained but small amounts (10), there was present in others the equivalent of 0.50 per cent calcium (9). From the earlier data of Joffe and McLean (21) it appears that in no case were more than 4.5 mgm. E. present in the soils they examined. Correspondingly low values were obtained by Kelley and Brown (24). The researches of Hissink (17), Gehring, Peggau, and Wehrmann (11), Osugi and Sano (28), and others, and the later investigations of Joffe and McLean (22), however, indicate that exchangeable hydrogen normally occurs in relatively considerable extent. The work of Bradfield (3), which suggests that complete saturation of clays with bases occurs only when a pH value of 10 or 11 is attained, lends indirect support to this view. If such is the case, hydrogen and calcium

together account for by far the greater majority of the exchangeable ions of the soils of humid climates, and upon the relative proportions of these two ions, and possibly also upon their absolute amounts, the properties of the soils will mainly depend.

The significance of the ratio of hydrogen ions to calcium ions has been realized by many workers, but comparatively few adequate attempts have been made to correlate it with either the behavior of the soil or its need for lime, probably because of the difficulties which underlie the accurate determination of the exchangeable hydrogen. To these difficulties the confusion which exists with regard to the soil content of ionizable hydrogen appears mainly to be due.

Hissink (16) at first avoided them by expressing the calcium ion (together with the other metallic ions) as a ratio of the clay and very fine silt, which he assumed to be a measure of the soil colloidal material and therefore of its saturation capacity. By means of such ratio values, soils in poor and in good condition can be distinguished, even though they differ widely in type and capacity for ion exchange (35). This method, however, is not sufficiently precise to reflect the gradation in soil properties caused by a relatively small change in ion content, unless the soils are otherwise very uniform in character. Later Hissink (17) determined the replaceable hydrogen by measuring the distribution of barium ions between varying amounts of decinormal barium hydroxide solution and a constant weight of soil. The results obtained were approximate, but the ratios they bore to the sum of the equivalents of the exchangeable ions present enabled him to differentiate between new, medium, and old soils of Holland.

The second method of Hissink has been subjected to much criticism on the following and other (34) grounds: (*a*) that side reactions may occur between the barium hydroxide solution and the soil, and that, consequently, an overestimation is made of the replaceable hydrogen present (24, 32); and (*b*) that alkaline soils of pH 9.2 to 10.2 give results by his titration process which indicate the occurrence of considerable amounts of replaceable hydrogen, whereas by his alternative conductometric method the same soils appear to be fully saturated with bases (32).

Gehring, Peggau, and Wehrmann (11) have shown that the ratio of exchangeable calcium to saturation capacity is related to the lime requirement of the soil and to the increase in crop yield following requisite liming. They determined saturation capacity by treating the soil with a saturated solution of calcium hydroxide, followed by heating to 60°C. After standing for 24 hours the soil suspension was saturated with carbon dioxide to precipitate the excess calcium hydroxide, and thoroughly boiled to decompose any calcium bicarbonate formed. The soil was then leached to two liters with normal sodium chloride solution, and its content of exchangeable calcium determined according to the method of Hissink. This procedure is open to objection because of the somewhat drastic treatment to which the soil is exposed. The inorganic and organic colloidal components of the soil are extremely reactive in character, and are readily subject to decomposition. Thorough boiling, therefore, may affect appreciably their capacity for ion exchange.

The ideas underlying the investigations of Hissink and of Gehring, Peggau and Wehrmann, in view of their extreme practical importance, merit wider application, and have been extended to the examination of soils of Trinidad. In view, however, of the objections made to their technique, alternative methods have been used. The work has been confined to the measurement of the ionizable hydrogen and calcium present in the soil, but a critical study has been made of the measures adopted, in order, if possible, to place the experimental procedure on a more firmly established basis.

PART I.—MEASUREMENT OF THE STATE OF UNSATURATION

DETERMINATION OF EXCHANGEABLE HYDROGEN AND CALCIUM

Joffe and McLean (21) and others have measured the exchangeable hydrogen present in soils by leaching them with neutral salt solution until the filtrates were no longer acid or contained no traces of calcium, and by titrating the extracts. Exact results are not given by such methods, for they involve the titration of small amounts of hydrogen ion in large volumes of solution. Page and Williams (29) overcame this difficulty by mixing the soil with calcium carbonate prior to leaching with sodium chloride solution. The hydrogen ions removed then interact with the carbonate, and an equivalent amount of calcium, which can be measured with precision, passes into solution. The method of Page and Williams, with some modifications, has been used in the present investigations.

Standard procedure adopted

The soils were air-dried and representative 25-gm. samples were intimately mixed with calcium carbonate, well moistened, treated with 100 cc. hot *N* NaCl, allowed to stand for some days, and then leached to two liters with this reagent. After the necessary correction was made for the calcium carbonate dissolved by, and originally present in, the leaching agent (0.038 gm., when expressed as calcium oxide, to the liter,), the total calcium passing into solution in the two liters was taken as a measure of the sum of the exchangeable hydrogen and calcium present in the soil sample. A discussion and fuller description of the method have been given in a previous paper (34).

The value thus obtained is an approximation to the total capacity of the soil for ion exchange, and for convenience is in future referred to as the saturation capacity (T). The soil content of exchangeable calcium (S) was separately estimated by the standard method of Hissink (16), and the replaced hydrogen, or, alternatively, the saturation deficit of the soil for calcium ions (T-S), was determined by difference. The ratio of exchangeable hydrogen to exchangeable calcium is expressed indirectly by means of the quotient $\frac{100\ (T\text{-}S)}{T}$. This ratio is termed, in accordance with current usage, "the degree of unsaturation of the soil with respect to calcium ions."

The procedure described for the determination of the exchangeable hydrogen and calcium together appears free from a main defect of the second method of Hissink (17) in that hydroxyl ions in high concentration are not brought into contact with the soil. It does not possess the disadvantage which characterises the technique of Bobko and Askinasi (2), Kelley and Brown (24), and Joffe and McLean (22). These workers replaced the ions originally present in the soil by those of one kind, removing all traces of the salt solution used by leaching with water. The protracted washing necessary may cause loss of the

replacing ion through solution of humates and hydrolysis. Further, it appears preferable to the method of Gehring, Peggau, and Wehrmann (11) in that, except for the initial use of hot sodium chloride, which can have but little heating effect upon the soil particles, the whole process is performed at normal temperature.

RELIABILITY OF THE METHOD

Effect of errors due to subsampling and technique

With methods of the type adopted it appears advisable to determine the extent to which the data obtained for the particular subsample examined are representative of the bulk sample from which it is taken, and also the extent to which they are affected by such deviations from a constant technique as may occur. Both possibilities of error are of particular importance in the determination of saturation deficit, which is not only measured by difference, but frequently possesses a small value. An endeavor therefore has been made to find the magnitude of the variations which may occur in the processes used. Three soils, each belonging to a different type, all of high saturation capacity, but containing approximately 0.1, 0.4, and 0.9 per cent exchangeable calcium, respectively, were selected for the purpose.

From the bulk samples of each of these soils six representative samples were obtained by the normal method. Three were leached to one liter for the determination of exchangeable calcium, and three, after the necessary preliminary treatment, were leached to two liters according to the standard procedure adopted for the measurement of saturation capacity. By determination of the calcium present in aliquot portions of each of the filtrates, two separate estimates (*a* and *b*, table 1) of the total calcium present in each liter were obtained. The estimation procedure followed was identical with that normally used in routine investigations. The data obtained for each soil were pooled (6) and the net standard deviations due to technique and subsampling, and the observed standard deviations, of the values obtained for its content of exchangeable calcium, its saturation capacity, saturation deficit, and degree of unsaturation were calculated. They are recorded in table 1.

The net standard deviations due to errors in technique of the values obtained for the contents of exchangeable calcium and the saturation capacities of the three soils examined are so small that they are negligible. They afford an excellent demonstration of the precision with which measurements of exchangeable calcium can be made by the method of Hissink (16) and of exchangeable calcium and hydrogen, together, by the modified method of Page and Williams, whether the quantities estimated are large or small. The net standard deviations due to errors in subsampling in the determination of exchangeable calcium (0.001 per cent CaO) are also very small, but in the case of saturation capacity they may attain a value of 0.012 per cent CaO. In both

determinations the errors due to subsampling are much larger than the errors due to technique, indicating that a closer estimate of the contents of exchangeable calcium and of saturation capacities of bulk samples could be obtained, with the same number of analytical measurements, by ignoring the errors due

TABLE 1

Errors due to subsampling and technique in determination of exchangeable calcium, saturation capacity, saturation deficit, and degree of unsaturation

SOIL TYPE*	DETERMINATION		SUBSAMPLE (I)	SUBSAMPLE (II)	SUBSAMPLE (III)	MEAN OF ALL	NET STANDARD DEVIATION DUE TO: Sub-sampling	NET STANDARD DEVIATION DUE TO: Tech-nique	OBSERVED STANDARD DEVIATION	OBSERVED S.D. AS PER CENT OF MEAN
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
G	Exchangeable calcium	(a)	0.112	0.109	0.111	.....	0.001	0.0003	0.001	1.2
		(b)	0.112	0.110	0.111	.....				
		Mean	0.112	0.110	0.111	0.111	.....	.....	.....	....
	Saturation capacity	(a)	0.906	0.929	0.924	.....	0.012	0.0003	0.012	1.3
		(b)	0.906	0.929	0.925	.....				
		Mean	0.906	0.929	0.925	0.920	.....	.....	.....	....
	Saturation deficit		.....	.....	.....	0.809	.....	.....	0.012	1.5
	Degree of unsaturation		.....	.....	.....	87.9	.....	.....	1.77	2.0
C	Exchangeable calcium	(a)	0.374	0.371	0.374	.....	0.001	0.0006	0.001	0.28
		(b)	0.374	0.373	0.373	.....				
		Mean	0.374	0.372	0.374	0.373	.....	.....	.....	....
	Saturation capacity	(a)	0.835	0.836	0.838	.....	0.001	0.0000	0.0015	0.18
		(b)	0.835	0.836	0.838	.....				
		Mean	0.835	0.836	0.838	0.836	.....	.....	.....	....
	Saturation deficit		.....	.....	.....	0.463	.....	.....	0.002	0.39
	Degree of unsaturation		.....	.....	.....	55.4	.....	.....	0.243	0.44
D	Exchangeable calcium	(a)	0.907	0.910	0.908	.....	0.001	0.0003	0.001	0.14
		(b)	0.907	0.909	0.908	.....				
		Mean	0.907	0.910	0.908	0.908	.....	.....	.....	....
	Saturation capacity	(a)	1.160	1.166	1.150	.....	0.009	0.001	0.010	0.82
		(b)	1.160	1.170	1.148	.....				
		Mean	1.160	1.168	1.149	1.159	.....	.....	.....	....
	Saturation deficit		.....	.....	.....	0.251	.....	.....	0.010	3.82
	Degree of unsaturation		.....	.....	.....	20.0	.....	.....	0.85	4.25

* A description of these soil types is given later in this paper.

to technique and making single analyses of the filtrates from double the number of subsamples. The observed standard deviations of the values for exchangeable calcium and saturation capacity in no case exceed 1.5 per cent when measured as percentages of the means.

The observed standard deviation recorded in table 1 for the saturation deficit

of each soil was calculated indirectly from the corresponding deviations for exchangeable calcium and saturation capacity. That for the degree of unsaturation was similarly obtained from the observed standard deviations of the saturation deficit and saturation capacity. The small variations which occur in the values for exchangeable calcium render the observed standard deviations for the saturation deficit but little larger than those for the corresponding saturation capacities. Neither the observed deviations for the saturation deficit nor the degree of unsaturation attain a value equal to 5 per cent of the mean, even when the saturation deficit and degree of unsaturation are as small as 0.25 per cent CaO and 20 per cent, respectively.

It appears from the data in table 1, therefore, that the mean values obtained by the standard procedure used, for exchangeable calcium, saturation capacity, saturation deficit, and degree of unsaturation, from duplicate estimations on a single subsample, give a sufficiently close approximation to those which would be obtained by the examination of a number of subsamples by this procedure, for most purposes of soil differentiation and characterization, but that when the significance of small differences is in question, three or more subsamples should be examined. The measurements obtained from a single subsample appear adequate for the investigations later described in this paper.

Effect of continued leaching on the values obtained

It is questionable whether leaching processes, as a class, displace from the soil all the hydrogen which can pass into the ionic form. Evidence of incomplete replacement by the modified method of Page and Williams has already been obtained (34). Further indications to the same effect are given by the pH values of the sodium clays[1] formed by the use of this method in determining the saturation capacities of the soils described in Part III of this paper. These values are recorded in column 4 of tables 3, 4, and 5. All of them lie between pH 7.70 and pH 8.37, a range which is much less alkaline in reaction than that obtained by Bradfield (3) for base-saturated soils. For these reasons an estimation has been made of the relative extent to which replacement of the ionizable hydrogen is limited by restricting the leaching process to two liters, and of the effect which partial replacement may exert upon the values for saturation capacity, saturation deficit, and degree of unsaturation when used for the purpose of soil differentiation and characterization.

Three soils, of high, medium, and low ionic capacity, respectively, the exchangeable calcium content of which had previously been determined, were selected from the various types later examined, and were leached to five liters with normal sodium chloride. With these soils certain modifications were introduced into the procedure used. After the soils were mixed with

[1] Previous to the determination of their pH values, these clays were not washed free from the sodium chloride solution used in their preparation. The sodium chloride present may repress the ionization of the sodium clays, thereby reducing their pH values.

calcium carbonate, treated with 100 cc. of hot salt solution, and allowed to stand, they were stirred, left to settle, and decanted 10 times with 50 cc. of cold salt solution previous to filtration. Instead of allowing them to remain in the funnels throughout the leaching process, they were removed to beakers after each separate liter had run through, stirred, and decanted 10 times as before, and then retransferred to funnels. The preliminary treatments of each soil, the decanting and leaching processes, and the subsequent analytical operations were performed side by side, in order that the data obtained for these soils should be strictly comparable. The calcium present in each liter

TABLE 2

Effect of continued leaching in determination of saturation capacity, saturation deficit, and degree of unsaturation

(*a*) *Saturation capacity and saturation deficit*

SOIL TYPE*	EXCHANGEABLE Ca	AMOUNT EXTRACTED BY					SATURATION CAPACITY		SATURATION DEFICIT		RATIO VALUES	
		Liter I	Liter II	Liter III	Liter IV	Liter V	Calculated from 1st 21 (T_2)	Calculated from 1st 51 (T_5)	Calculated from 1st 21 (T_2-S)	Calculated from 1st 51 (T_5-S)	$\frac{T_2}{T_5}$	$\frac{T_2-S}{T_5-S}$
	Gm. CaO per 100 gm. air-dry soil											
F	0.069	0.141	0.024	0.014	0.008	0.001	0.165	0.188	0.096	0.119	0.88	0.81
G	0.222	0.596	0.118	0.064	0.044	0.044	0.714	0.866	0.492	0.644	0.82	0.76
B	0.315	0.732	0.122	0.080	0.062	0.058	0.854	1.054	0.539	0.739	0.81	0.73

(*b*) *Degree of unsaturation*

SOIL TYPE	DEGREE OF UNSATURATION (PER CENT) CALCULATED FROM					RATIO VALUES			
	Liter I U_1	1st 21 U_2	1st 31 U_3	1st 41 U_4	1st 51 U_5	$\frac{U_1}{U_5}$	$\frac{U_2}{U_5}$	$\frac{U_3}{U_5}$	$\frac{U_4}{U_5}$
F	51.1	58.2	61.5	63.1	63.3	0.81	0.92	0.97	1.00
G	62.8	68.9	71.5	73.0	74.4	0.84	0.93	0.96	0.98
B	57.0	63.1	66.3	68.4	70.1	0.81	0.90	0.95	0.98

* A description of these soil types is given later in this paper.

of filtrate was determined in duplicate. As the amount of calcium carbonate dissolved was found to be unaltered by the modifications introduced, the customary adjustments were made, for each of the five liters, for its solubility in the leaching agent. The corrected mean values obtained are given in table 2. To avoid confusion the amounts of calcium passing into solution through exchange reactions with the soil in two liters and five liters are for the time being termed the "apparent" and "proximate" saturation capacities, respectively. The corresponding saturation deficits and degrees of saturation are similarly designated.

The data in table 2 show that far larger amounts of hydrogen are replaced

by the first liter of filtrate than by each subsequent liter; that fairly large quantities are extracted by the second liter; and that significant amounts may be removed by the third, fourth, and fifth liters. The amounts displaced by liters III, IV and V from the soil of low saturation capacity (0.014, 0.008, and 0.001 per cent CaO respectively,) are small. They demonstrate that ion exchange in this soil is, for practical purposes, complete when five liters of filtrate have been obtained; and they confirm, to some extent, the validity of the correction used for the solubility of calcium carbonate in the leaching agent. The quantities present in liters III, IV, and V together, become increasingly important, however, as the degree of colloidality of the soil increases. They amount to 0.15 per cent CaO for the soil of medium saturation capacity and 0.20 per cent CaO for the soil of highest saturation capacity. Such data suggest that the greater the capacity of the soil for ion exchange, the greater is the volume of filtrate necessary completely to remove the ionizable hydrogen. As the quantities present in liters IV and V of the filtrate from both the heavier soils differ but little in magnitude, leaching to an indefinite volume appears to be required for this purpose.

The pH values of the sodium clays formed by leaching the three soils of types F, G, and B to five liters were found to be 8.37, 8.25, and 8.28, respectively. In spite of the continued leaching, these values are much lower than those obtained by Bradfield (3) for base-saturated soils. It is perhaps noteworthy that Osugi and Sano (28) found the soils they examined to be saturated at values ranging from pH 8.6 to 11.

DISCUSSION

It is clear from the data accumulated that the replacement resulting from leaching to two liters by the modified method of Page and Williams can be only partial in character. Complete replacement, however, need not necessarily be essential for the object of soil differentiation and characterization, provided that for each soil: (*a*) constant results for the amount of calcium and hydrogen replaced are obtained on repetition; (*b*) the ratios of the apparent saturation capacity, saturation deficit, and degree of unsaturation to their respective true values are independent (i) of the magnitude of the saturation capacity of the soil and (ii) of the nature of the colloidal material of the type from which the soil is drawn; and (*c*) exchange of hydrogen occurs to such an extent that the ratios of the replaced hydrogen to calcium in good and poor soils are sufficiently different adequately to reflect the dissimilarity in their properties.

The data given in table 1 demonstrate that the first of these stipulations is satisfied, in that the measurements of saturation capacity and saturation deficit obtained on repetition are in close accordance.

There are given in table 2 *a* the apparent and proximate saturation capacities (denoted by T_2 and T_5, respectively,) and saturation deficits [$(T_2 - S)$ and $(T_5 - S)$] of the three soils leached to five liters. From them the ratio

values $\frac{T_2}{T_5}$ and $\frac{T_2 - S}{T_5 - S}$ have been calculated. The data obtained demonstrate that the ratio of the apparent to the proximate saturation capacity $\frac{T_2}{T_5}$ varies from 0.88 for the soil of lowest saturation capacity to 0.81 for the soil of highest saturation capacity. The difference between these values is smaller than that between the ratios of the apparent to the true saturation capacities for these soils, for, as table 2 indicates, further leaching would remove greater quantities of ion from the soil of high than of low saturation capacity. Assuming that the standard deviation of the values obtained for the apparent and proximate saturation capacities are in each case equal to 1.3 per cent of their means (the maximum deviation found for the saturation capacities recorded in table 1), the standard error of the difference between the ratio values 0.88 and 0.81 is 0.022. It appears, therefore, that the percentage of the sum equivalent of the calcium and hydrogen ions present, which are removed by the first two liters of filtrate, decreases significantly as the saturation capacity increases in magnitude.

The pH values of the sodium clays recorded in tables 3, 4, and 5 tend to confirm this conclusion, in that they exhibit a fairly well-defined propensity to decrease with increasing saturation capacity. The correlation coefficient of the pH values of these clays with their saturation capacities, for the 49 soils for which both sets of data have been obtained, is -0.490, $P = <0.01$. The corresponding correlation coefficient for the 15 soils of type G is -0.548, $P = <0.05$.

A similar state of affairs holds for the measurements of saturation deficit. Eighty-one per cent of the hydrogen ions extracted by five liters of filtrate are present in the first two liters from the soil of lowest saturation capacity, 76 per cent from the soil of medium saturation capacity, and only 73 per cent from the soil of highest saturation capacity. If the standard deviations of the values for the saturation deficits of the soils of minimum and maximum saturation capacity are taken in this case as equal to 2 per cent of their respective means, the standard error of the difference of their ratio values amounts to 3.1 per cent. The difference of 8 per cent is significant under such circumstances. As before, this difference would be greater if the measurements for the proximate saturation deficits were replaced by those for the true saturation deficits.

This lack of consistency in the values of the ratios $\frac{T_2}{T_5}$ and $\frac{(T_2 - S)}{(T_5 - S)}$ may be attributed to differences in the nature of the colloidal material of the soils examined. Another explanation is that the leaching solution comes into equilibrium with the soil solution more quickly with soils of low than of high saturation capacity, and that, although the soil is transferred to a beaker after each liter has run through, and thoroughly stirred and decanted 10 times before leaching

is continued, equilibrium conditions are not attained with soils of higher saturation capacity. If these are the contributory causes, there can be little doubt that in the determination of saturation capacity and saturation deficit the leaching process should be continued until as large a volume of filtrate as practicable is obtained.

TABLE 3

Lime status and physical constants of soils in good condition (Group I)

1	2	3	4	5	6	7		8		9		10	11
SOIL TYPE	SOIL NUMBER	pH VALUE	pH VALUE OF Na CLAY	C. + F.S.*	$CaCO_3$	SATURATION CAPACITY (T) (Per 100 gm. air-dry soil)		EXCHANGEABLE Ca (S) (Per 100 gm. air-dry soil)		SATURATION DEFICIT (T-S) (Per 100 gm. air-dry soil)		DEGREE OF UNSATURATION $[100(T-S)/T]$	$\frac{S}{C. + F.S.*}$
				per cent	per cent	gm. CaO	mgm. E.	gm. CaO	mgm. E.	gm. CaO	mgm. E.		
Naparima District													
C	M. 64	7.14	7.81	45.32	0.28	0.588	21.00	0.470	16.80	0.118	4.20	20.1	0.37
	M. 101	7.51	8.01	58.53	Trace	0.700	25.00	0.547	19.54	0.153	5.46	21.9	0.33
D	M. 181	7.22	7.90	62.38	0.05	1.087	38.82	0.935	33.39	0.152	5.43	14.0	0.54
	M. 40	5.69	7.86	63.60	0.00	0.996	35.57	0.810	28.93	0.186	6.64	18.7	0.45
E	MPD. 7	7.48	7.90	53.05	0.14	1.150	41.07	0.919	32.82	0.231	8.25	20.1	0.62
	M. 42	5.84	7.87	60.00	Trace	1.717	61.32	1.298	46.36	0.419	14.96	24.4	0.77
Central Plain													
G	CA. 15	6.83	7.86	55.17	Trace	0.572	20.43	0.439	15.68	0.133	4.75	23.2	0.28
	B. 39	6.35	8.16	20.00	0.02	0.548	19.57	0.414	14.79	0.134	4.78	24.5	0.74
	CPD. 1	7.87	8.13	22.03	Trace	0.354	12.64	0.256	9.14	0.098	3.50	27.7	0.41
	CA. 16	7.44	8.04	23.99	Trace	0.390	13.93	0.279	9.96	0.111	3.97	28.5	0.42
H	O. 59	6.91	7.93	36.25	Trace	0.420	15.00	0.369	13.18	0.051	1.82	12.1	0.36
	A. 10	7.66	7.70	18.57	Trace	0.247	8.82	0.205	7.32	0.042	1.50	17.0	0.39
Mean value												21.0	....

*C = clay; F.S. = fine silt.

A third possibility exists, however, namely, that side and secondary reactions, negligible in extent in soils of low saturation capacity, but appreciable in soils of higher saturation capacity, occur during the later stages of the leaching process. Such reactions could be due to: the hydroxyl ions released by hydrolysis of the sodium clay; decomposition of the sodium clay, which is possibly somewhat unstable; and increased hydration of the components of the colloidal complex through continued contact with an aqueous solution. All would tend to increase the value for the saturation capacity. Of these

alternatives the third appears the most probable. The effect of the first is likely to be very small, for ionization of the sodium clay should be almost completely suppressed by the high concentration of sodium ions in the normal salt solution in contact with the soil.

In the investigations later described, leaching was restricted to two liters, partly to economize in time and material and partly to minimize the effect of possible side and secondary reactions. It is necessary to bear in mind, however, that the values thus obtained for saturation capacity and saturation deficit may not be strictly comparable.

TABLE 4

Lime status and physical constants of transition soils (Group II)

1	2	3	4	5	6	7		8		9		10	11
SOIL TYPE	SOIL NUMBER	pH VALUE	pH VALUE OF Na CLAY	C. + F.S.*II	$CaCO_3$	SATURATION CAPACITY (T)		EXCHANGEABLE Ca (S)		SATURATION DEFICIT (T-S)		DEGREE OF UNSATURATION $[100(T\text{-}S)/T]$	$\frac{S}{C. + F.S.*II}$
						(Per 100 gm. air-dry soil)							
				per cent	*per cent*	gm. CaO	mgm. E.	gm. CaO	mgm. E.	gm. CaO	mgm. E.		
Naparima District													
B	M. 24	5.31	7.79	.....	0.00	0.679	24.25	0.468	16.71	0.211	7.54	30.9	....
	M. 48	6.55	7.83	.....	0.00	0.664	23.71	0.433	15.46	0.231	8.25	34.8	....
C	M. 71	6.07	7.92	34.63	0.00	0.553	19.75	0.370	13.21	0.183	6.54	33.1	0.38
D	M. 190	6.39	7.78	67.50	0.00	0.930	33.21	0.622	22.21	0.308	11.00	33.1	0.33
Central Plain													
G	W. 48	6.68	7.97	56.00	0.00	0.698	24.93	0.472	16.86	0.226	8.07	32.4	0.30
H	O. 122	6.89	7.97	29.10	0.00	0.329	11.75	0.230	8.21	0.099	3.54	30.1	0.28
Mean value.....												32.4	....

*C = clay; F.S. = fine silt.

The degree of unsaturation, as calculated on the basis of a one, two, three, four, and five liter extraction, for the three soils examined is recorded in table 2 *b*. The five values obtained for each soil are denoted by U_1, U_2,.... U_5, respectively, in this table. The difference between U_1 and U_5 amounts to between 11 and 13 per cent for each of the soils examined. This difference is very substantial, and by comparison with the observed standard deviations of the values for the degrees of unsaturation recorded in table 1, is undoubtedly significant. The two-liter values (U_2) lie in each case approximately midway between the extreme values obtained (U_1 and U_5).

The ratios which U_1, U_2, U_3, and U_4 bear to U_5 are also given in table 2*b*. The three values for $\frac{U_1}{U_5}$ approximate closely a constant 0.82. Those for $\frac{U_2}{U_5}$

TABLE 5

Lime status and physical constants of soils in poor condition (Group III)

	1	2	3	4	5	6	7		8		9		10	11
	SOIL TYPE	SOIL NUMBER	pH VALUE	pH VALUE OF Na CLAY	C. + F.S.* H	$CaCO_3$	SATURATION CAPACITY (*T*)		EXCHANGEABLE Ca (*S*)		SATURATION DEFICIT (*T-S*)		DEGREE OF UNSATURATION $[100(T-S)/T]$	$\frac{S}{C.+F.S.*H}$
							(Per 100 gm. air-dry soil)							
					per cent	*per cent*	gm. CaO	mgm. E.	gm. CaO	mgm. E.	gm. CaO	mgm. E.		
							Naparima District							
A		MH. 15	5.31	7.70	74.60	0.00	0.737	26.32	0.401	14.32	0.336	12.00	45.6	0.19
A		M. 50	5.04	7.73	62.67	0.00	0.828	29.57	0.431	15.39	0.397	14.18	48.0	0.25
B		M. 22	5.63	7.88	.....	0.00	0.611	21.82	0.359	12.82	0.252	9.00	41.2	....
B		M. 25	4.93	7.83	.....	0.00	0.810	28.93	0.460	16.43	0.350	12.50	43.2	....
B		M. 27	5.79	8.00	.....	0.00	0.579	20.68	0.320	11.43	0.259	9.25	44.7	....
B		M. 44	4.92	7.88	.....	0.00	0.714	25.50	0.305	10.89	0.409	14.61	57.3	....
B		MPD. 9	5.03	8.17	57.50	0.00	0.800	28.57	0.315	11.25	0.485	17.32	60.6	0.20
B		M. 29	4.53	7.78	.....	0.00	0.581	20.75	0.221	7.89	0.360	12.86	62.0	....
B		M. 23	4.53	7.84	.....	0.00	0.790	28.21	0.300	10.71	0.490	17.50	62.0	....
B		M. 179	4.72	7.83	67.62	0.00	0.699	24.96	0.210	7.50	0.489	17.46	70.0	0.11
B		M. 30	4.58	7.79	.....	0.00	0.597	21.32	0.150	5.36	0.447	15.96	74.9	....
C		M. 151/152	5.20	7.75	51.59	0.00	0.545	19.46	0.307	10.96	0.238	8.50	43.7	0.21
C		M. 38	5.32	7.88	37.80	0.00	0.553	19.75	0.245	8.75	0.308	11.00	55.7	0.23
C		M. 156	4.48	.....	59.50	0.00	0.785	28.04	0.219	7.83	0.566	20.21	72.1	0.13
							Central Plain							
F		A. 49	6.87	8.21	12.38	0.00	0.126	4.50	0.075	2.68	0.051	1.82	40.5	0.22
F		A. 50	6.31	8.28	14.38	0.15	0.152	5.43	0.069	2.46	0.083	2.97	54.6	0.17
F		A. 66	5.61	8.13	41.88	0.00	0.463	16.54	0.176	6.29	0.287	10.25	62.0	0.15
F		A. 57	6.00	8.17	15.13	0.00	0.255	9.11	0.089	3.18	0.166	5.93	65.1	0.21
F		A. 56	5.93	8.37	13.63	0.00	0.244	8.71	0.075	2.68	0.169	6.03	69.2	0.20
G		W. 62	6.15	7.91	56.25	0.00	0.739	26.39	0.455	16.25	0.284	10.14	38.4	0.29
G		CPD. 3	6.30	7.95	52.02	0.00	0.562	20.07	0.309	11.04	0.253	9.03	45.0	0.21
G		CA. 2	4.77	7.75	75.75	0.00	0.860	30.71	0.380	13.57	0.480	17.14	55.8	0.18
G		W. 106	4.72	7.80	70.00	0.00	0.716	25.57	0.315	11.25	0.401	14.32	56.0	0.16
G		WOA. 341	6.06	8.04	7.12	0.00	0.220	7.86	0.094	3.36	0.126	4.50	57.3	0.47
G		WOPD. 5	4.91	8.26	55.12	0.00	0.537	19.18	0.222	7.93	0.315	11.25	58.7	0.14
G		B. 21	5.36	8.15	30.70	0.00	0.549	19.61	0.217	7.75	0.332	11.86	60.5	0.25
G		CA. 1	4.70	7.74	77.90	0.00	0.965	34.46	0.364	13.00	0.601	21.46	62.3	0.16
G		B. 25	4.98	8.12	22.35	0.00	0.398	14.21	0.144	5.14	0.254	9.07	63.8	0.23
G		WOPD. 3	5.06	8.07	51.62	0.00	0.647	23.11	0.179	6.39	0.468	16.72	72.3	0.12
H		WOA. 320	6.41	7.99	43.10	0.00	0.525	18.77	0.301	10.75	0.224	8.02	42.7	0.25
H		WOA. 339	6.14	7.89	38.00	0.00	0.539	19.25	0.251	8.96	0.288	16.37	53.4	0.23
H		WOA. 332	6.49	8.12	38.00	0.00	0.501	17.89	0.194	6.93	0.307	10.96	61.3	0.18
	Mean value.....												56.2	

* C = clay; F.S. = fine silt.

$\frac{U_3}{U_5}$ and $\frac{U_4}{U_5}$ differ but little from 0.92, 0.96 and 0.99, respectively. The differences between the three values for each ratio are not significant, unless the standard deviations of U_1, U_2,.... U_5 are each less than 1 per cent when calculated as percentages of the means. The consistency exhibited by the members of each set of the successive ratio values $\frac{U_1}{U_5}$, $\frac{U_2}{U_5}$, $\frac{U_3}{U_5}$, and $\frac{U_4}{U_5}$ together with the fact that measurements of the degree of unsaturation can be reproduced with fair exactness, suggests that they can be used with a reasonable degree of accuracy for the comparative differentiation and characterization of soils, even though they are calculated from data obtained by incomplete extraction. Further, as the values for $\frac{U_1}{U_5}$, for the three soils examined differ no more greatly from one another than those for $\frac{U_2}{U_5}$, $\frac{U_3}{U_5}$, or $\frac{U_4}{U_5}$, little appears to be gained by continuing the leaching process beyond one liter of filtrate for comparative measurements of this soil factor. In the investigations subsequently described it has been determined on the basis of a 2-liter extraction, for the sake of uniformity with the measurements of saturation capacity and saturation deficit.

The data recorded in tables 3, 4, and 5 demonstrate that the values obtained for the degree of unsaturation, during the routine examination of a large number of soils, cover a wide and satisfactory range. The procedure adopted therefore complies with the third of the conditions regarded as necessary for its use in soil classification.

PART II.—STATE OF UNSATURATION OF THE SOIL IN RELATION TO ITS FIELD BEHAVIOR

DESCRIPTION AND CLASSIFICATION OF THE SOILS EXAMINED

The sugar-cane regions of Trinidad were deemed ideal for the investigation of any relationship which may exist between the state of unsaturation of the soil and its field behavior and lime requirement, first, because of the extreme variations in soil type, and in some cases within the soil type, which occur in a restricted area; and secondly, because one crop is common to them all. Samples, taken to a depth of one foot, representative of the following eight distinct geological types were chosen for examination. Some of these types have been previously described (35).

Soil types of the Naparima District

A. A brown, raw clay, characterized by the greenish hue of its partially weathered subsoil. It is for the most part foraminiferal.

B. A typical, red-weathering, foraminiferal clay, which frequently merges imperceptibly into the previous type.

C. An old river alluvium, yellow-brown.
D. A recent river and lagoon alluvium, dark brown.
E. A black soil, overlying a buff colored calcareous marl.

Soils of the Central Plain

F. Red-brown detritus soils, bordering on the foothills of the Northern Range, and derived from the Pre-Cretaceous quartzose schists of which the range is mainly formed.
G. Fawn colored, one-time swamp and lagoon alluvial soils, which merge into present-day swamps.
H. Dark brown, recent river alluvial soils.

All the foregoing types are essentially alumino-siliceous in character and are very deficient in organic matter (35). Some of them have been more fully described by Hardy (15).

System of classification

The samples obtained from the eight soil types are classified into three groups, according to their field behavior:

Group I. Soils possessing an inherent good tilth.
Group II. Soils with neither markedly good nor bad properties, but which are beginning to exhibit the characteristics of physical deterioration, and are at present in the transition stage from the first to the third groups.
Group III. Soils in a badly impaired condition, to which, at the best, a temporary good tilth only can be given.

The climatic conditions prevailing in Trinidad emphasize the differences in behavior of the soils of groups I and III and render them readily distinguishable. Briefly it may be stated that the latter exhibit marked fluctuations in behavior from the dry to the wet season, appear to be poorly aerated, and are in obvious need of flocculation. The variation in behavior of the former from season to season is much less pronounced, and they possess, throughout the year, as good a tilth as climatic conditions and their content of organic matter appear to allow. A further and almost invariable distinction is that the soils of the third group support sugar canes periodically subject to severe injury from an insect pest—*Monecphora* (*Tomaspis*) *saccharina* Dist. (the frog-hopper)—from which those grown on the soils of the first group are almost completely free. Recently in years of serious insect infestations, canes grown on the second group have been subject to slight damage in this manner.

In addition to the measurements necessary for the determination of the state of unsaturation of the soils of the three groups, the following determinations were made:

pH value was measured on duplicate representative samples of each soil by means of the quinhydrone electrode. A soil-water ratio of 1 to 2 was used.

The soil content of *clay and very fine silt* was determined previous to the publication of the

recommendations of the Agricultural Educational Association in 1928. It was measured according to the procedure adopted by this body in 1925. The necessary corrections for temperature were made.

Calcium carbonate was estimated by means of Collin's calcimeter.

The data obtained for 50 samples, selected from those examined as representative of the good, transitional, and poor soils of the eight types described in the foregoing, are summarized in tables 3, 4, and 5, respectively. The soils of each group are arranged in order of increasing degree of unsaturation. Type B, which is fairly uniform in saturation capacity, and type G, which is very variable in this respect, because of their diverse origin, are more fully exemplified than the other types.

TABLE 6

Distribution of saturation capacities (T), contents of exchangeable calcium (S) and saturation deficits (T-S) of soils of Groups I, II, and III

CaO per 100 gm. air-dry soil	Soils in good condition Group I			Transition soils Group II			Soils in poor condition Group III		
	T	*S*	*T-S*	*T*	*S*	*T-S*	*T*	*S*	*T-S*
0.0–0.1	0	0	3	0	0	1	0	5	2
0.1–0.2	0	0	7	0	0	1	2	5	3
0.2–0.3	1	3	1	0	1	3	3	7	9
0.3–0.4	2	1	0	1	1	1	1	11	8
0.4–0.5	1	3	1	0	3	0	1	4	8
0.5–0.6	3	1	0	1	0	0	11	0	1
0.6–0.7	0	0	0	3	1	0	3	0	1
0.7–0.8	1	0	0	0	0	0	6	0	0
0.8–0.9	0	1	0	0	0	0	4	0	0
0.9–1.0	1	2	0	1	0	0	1	0	0
>1.0	3	1	0	0	0	0	0	0	0
Total....	12			6			32		

SATURATION CAPACITY, EXCHANGEABLE CALCIUM, AND SATURATION DEFICIT

The distribution of the saturation capacities, the contents of exchangeable calcium, and the saturation deficits of the soils of groups I, II, and III are recorded in table 6.

Saturation capacity

The saturation capacities of the soils of group I are fairly evenly scattered between the values 0.25 and 1.7 gm. CaO per 100 gm. of air-dry soil; those for the soils of group II range from 0.3 to 1.0 per cent; whereas the majority of the values for the soils of group III lie between 0.5 and 0.9 per cent. No regular relationship appears to exist between field behavior of the soil and the magnitude of the saturation capacity, provided it is greater than 0.25 per cent

CaO. High saturation capacities, such as are characteristic of types A and B and some of the soils of type G, are not necessarily correlated with poor physical condition, for the soils of type E, which possess even higher saturation capacities, retain their tilth throughout the year more markedly than do any of the soils of the other seven types. Between poor condition and low ion capacity there may be some connection. The minimum saturation capacity found for the good and transitional soils is 0.25 per cent CaO. The behavior of the soils which possess values below this amount suggests that their condition is in part due to the lack of sufficient colloidal material successfully to withstand the climatic conditions which prevail.

Exchangeable calcium

The contents of exchangeable calcium of the soils examined range from 0.075 to 1.298 gm. CaO per 100 gm. of air-dry soil. This range is greater than that found by Williams (37) for Welsh soils (0.07 to 0.28 per cent CaO), by Smith (33) and Ogg and Dow (27) for Scottish soils (0.04 to 0.55 per cent CaO), by Kelley and Brown (23) for American soils (0.12 to 0.92 per cent CaO), and by Hissink (16) for Dutch soils (0.21 to 1.12 per cent CaO).

The content of the soils in good condition may rise above 1.0 per cent CaO, whereas the maximum values recorded for the transition and poor soils examined are 0.7 and 0.5 per cent, respectively. Apart from these limiting cases there is little evidence of a relationship between the absolute amount of exchangeable calcium present and field behavior. This appears to be mainly due to the variation which exists in the saturation capacities of the soils examined, for an increase in the capacity for ion exchange of the good soils is invariably accompanied by a concurrent increase in their contents of exchangeable calcium.

Saturation deficit

To some extent account is taken, in the determination of saturation deficit, both of the saturation capacity of the soil and of its content of exchangeable calcium. A closer relationship therefore may be expected between it and soil behavior than exists in the case of either of the factors from which it is derived. Certain investigators have used it as a measure of the lime requirement of the soil. Those methods for determining lime requirement which involve the estimation of the acidity developed by the soil in the presence of neutral salt solutions are based upon qualified measurements of its value. The degree to which the magnitude of the saturation deficit is linked with the field behavior of the soils examined is therefore worthy of detailed consideration.

The saturation deficits registered in tables 3, 4, and 5 vary from 0.04 to 0.60 gm. CaO per 100 gm. of air-dry soil; those for the soils of group I lie between 0.04 and 0.42 per cent CaO; whereas the values for the soils of group III cover the whole of the recorded range. In the great majority of cases, however, the

saturation deficits of the soils of the former group are less than 0.20 per cent CaO, whereas those for the soils of the latter group are in general larger than this. The deficits of the transition soils are ranged about this value, varying from 0.10 to 0.31 per cent CaO. A loose relationship, therefore, appears to exist between the saturation deficits of the soils as a whole and their field behavior, but the overlap which occurs in the values for individual soils of the different groups renders the connection too ill defined to warrant a formulated generalization. The lack of precise definition which obtains is well illustrated by the following specific examples. Soil M 42 of type E, group I, has a saturation deficit (0.42 per cent CaO) greater than the values for all the soils of group II and for most of the soils of group III. Similarly, the deficits of soils A 49 and A 50, of type F, group III, (0.05 and 0.08 per cent CaO, respectively) are smaller than those for the vast majority of the soils of groups I and II. These are extreme cases, but many examples similar in kind, though of lesser degree, appear in the tables.

The data obtained nevertheless demonstrate that in special cases, such as those for soils confined to a single type which is of fairly uniform saturation capacity throughout, a close relationship may exist between saturation deficit and field behavior. For example, the minimum deficit found for the poor soils of type C is 0.24 per cent CaO, the transition soil has a value of 0.18, and the good soils of this type possess deficits which range from 0.12 to 0.15 per cent CaO. The soils of the different groups of types B and H exhibit a similar gradation in their limiting values. When, however, the saturation capacity of the type is very variable, the relationship becomes less well defined. In the case of type G, the poor soils have a minimum deficit of 0.13, the good soils a maximum deficit of 0.14, and the transition soil cited possesses the value 0.23 per cent CaO.

It is evident from these examples that, as in the case of exchangeable calcium, the relationship between the magnitude of the saturation deficit and the field behavior of the soil is obscured by the variation which occurs in the capacity of the soil for ion exchange. If the saturation capacity is very high, a deficit of 0.4 per cent CaO is not incompatible with inherent good tilth. If, on the other hand, it is very low, as small a deficit as 0.05 per cent CaO may be correlated with poor condition. It follows that the saturation deficit cannot, in general, be regarded as a reliable index of soil condition.

DEGREE OF UNSATURATION

The degree of unsaturation of the soils examined varies from 12 to 88 per cent (tables 1, 3, 4, and 5). This range is wider than that found by Hissink (17) for Dutch soils (44 to 74 per cent), by Joffe and McLean (22) for American soils (12 to 63 per cent) and by Osugi and Sano (28) for Japanese soils (17 to 77 per cent).

The extent to which the Trinidad soils classified in group III have become

unsaturated appears independent of internal factors such as the magnitude of their saturation capacity and the nature of the type to which they belong. No evidence exists that the light soils of type G, for example, are in general more highly unsaturated than its heavy soils, or that the soils of type F are less saturated than those of type B.

Although no close connection exists in general between the field behavior of the soil and its absolute content of exchangeable hydrogen or calcium, the data in tables 3, 4, and 5 show it to be intimately related to their ratio value. The soils in good condition, those with a somewhat impaired tilth, and the poor soils each lie within a fairly well-defined zone of unsaturation. The degree of unsaturation of the soils in good condition ranges from 12 to 28 per cent, with a mean value of 21 per cent. The limits of unsaturation of the transition soils are 30 and 35 per cent, with a mean value of 32 per cent. The soils in poor condition are more than 38 per cent unsaturated.

The delimiting values of the three zones appear to be independent of the following factors:

The nature of the colloidal material of the soils examined, as determined by the type to which they belong. Each range of values holds for the soils of all eight types, in spite of their diverse origin.

The degree of the colloidality of the soils, whether measured by their saturation capacity or their content of clay and fine silt. The soils of the very variable type G are as precisely differentiated according to their condition as the soils of the more uniform types.

Any variation which occurs in the content of exchangeable ions, other than hydrogen and calcium, of the soils examined.

The agricultural history of these soils, which in some cases have grown cane for generations, whereas others have until recently supported cacao.

The degree of unsaturation with calcium, i.e., the ratio of exchangeable hydrogen to calcium, therefore appears to be a master factor controlling the field behavior of these soils.

It is known that humus, if present in large quantities, may dominate the properties of the soil and mask the effect of the exchangeable ions, but that, if it occurs to a small extent, the nature of its influence is largely dependent upon their relative proportions. The amount of organic colloidal material found in the soils of the cane-growing regions is relatively small compared with the high degree of inorganic colloidality possessed by many of these soils (35). This may aid in emphasizing the measure of control over the soils examined which the degree of unsaturation exhibits, and may afford an explanation of the comparative precision with which the zones of unsaturation are defined. It is noteworthy in this respect that Gehring, Peggau, and Wehrmann (12) found that lime requirements, based on their method of determining the degree of saturation, are applicable to mineral but not humic soils.

It has been shown in a previous paper (35) that the soils of Trinidad in poor condition are distinguished from those in good condition by the ratio of the amount of exchangeable calcium present in them to their content of clay and

very fine silt (C. + F.S. II). The ratios for the former soils were found to range from 0.11 to 0.25, and those for the latter from 0.28 to 0.63. The ratios for the extended series of soils, recorded in column 12 of tables 3 and 5, confirm these findings. They vary from 0.11 to 0.29 for the soils of group III and from 0.28 to 0.68 for those of group I. The contrasted soils are not so clearly differentiated by this means, however, as by their degree of unsaturation, for the ratios for the transition soils, which vary from 0.28 to 0.38, lie within the range for the good soils. Further, the poor soil WOA 341 of type G, originally found to be an exception in that it has a ratio value of 0.47, possesses a degree of unsaturation of 57 per cent, a value well within the zone corresponding to the soils of group III.

Hissink (19) found the ratio of exchangeable calcium to clay and very fine silt for Dutch soils to be highly correlated with their degree of saturation.

TABLE 7

Degree of unsaturation of new, medium, and old Dutch soils

[Recalculated from the data of Hissink (17)]

	AGE OF SOIL								
	New			Medium	Old and very old				
Soil number	B1681	B1459	B1680	B1679	B790	B1482	B1483	B1484	B1458
100 $(T\text{-}S)/T$									
Hissink's value	43.6	47.2	45.5	48.0	53.2	61.2	59.2	55.3	74.2
Recalculated value	49.2	52.8	51.1	53.6	58.7	66.4	64.5	60.8	78.2
pH value	7.61	7.57	7.70	7.67	7.03	5.89	5.96	6.25	7.49
Humus (per cent.)	0.0	0.7	0.0	1.5	3.2	3.4	3.1	2.1	0.0
$CaCO_3$ (per cent)	10.6	9.3	3.2	0.7	0.0	0.0	0.0	0.0	0.0

The correlation of $\frac{S}{(C. + F.\ S.\ II)}$ with $\frac{100\ (T - S)}{T}$ for the 41 Trinidad soils for which both sets of values have been obtained is -0.726, with $P = <0.01$.

COMPARISON WITH RESULTS OF HISSINK

Hissink (17) included the soil content of exchangeable sodium, potassium, and magnesium in his measurement of saturation capacity. For the purpose of comparison his data have been recalculated on the assumption that calcium and hydrogen alone are present. The recalculated degrees of unsaturation are each greater than the original values by from 4 to 6 per cent.

The zones of unsaturation of the new and old soils of Holland are limited by the values 49 and 53 per cent, and 58 and 78 per cent, respectively. Although the new soils contain calcium carbonate, their degree of unsaturation lies well within the zone which characterizes the poor soils of the cane-growing regions of Trinidad. It is clear, therefore, that the method of Hissink for determining

the soil content of exchangeable hydrogen gives much higher values than the modified method of Page and Williams.

It is doubtful whether the divergence can be explained either by the difference in the humus contents of the two series of soils—for the contents of the Dutch soils, which were determined by loss in weight on ignition, are the smaller—or by the difference in the length of time allotted to replacement in the two processes. In the modified method of Page and Williams the leaching process alone, in which the soil is repeatedly brought into contact with fresh sodium chloride solution, normally takes at least 3 days.

To investigate the reason for the discrepancy, the saturation deficits of the three soils of types F, G, and B, samples of which had previously been leached to five liters, were determined by the method of Hissink. The procedure followed was identical with that described by him. In each case the amount of soil taken was such that it contained approximately 2 gm. of the clay fraction. The soils were placed in a series of test tubes and increasing quantities (5, 10, 15 .... 45 cc.) of 0.1 N $Ba(OH)_2$ added. Each tube was filled with water to 50 cc., shaken occasionally for three days, and then allowed to settle overnight. A portion of the clear supernatant liquid was pipetted off and titrated with standard hydrochloric acid, phenolphthalein being used as the indicator. From the data obtained the saturation deficits of the three soils were calculated. Their values, together with those obtained by their use for the saturation capacity and degree of unsaturation, are compared in table 8 with the corresponding values given by the modified method of Page and Williams on the basis of 2- and 5-liter extractions.

TABLE 8

Values for $(T\text{-}S)$, T, *and* $\frac{100\,(T\text{-}S)}{T}$ *as determined by the method of Hissink and by the modified method of Page and Williams*

(2- and 5-liter extractions)

SOIL TYPE	METHOD OF HISSINK			MODIFIED METHOD OF PAGE AND WILLIAMS						RATIO OF VALUES FOR $(T\text{-}S)$	
	1	2	3	4	5	6	7	8	9		
				2 liter extraction			5 liter extraction				
	$(T\text{-}S)$	T	$\frac{100(T\text{-}S)}{T}$	$(T\text{-}S)$	T	$\frac{100(T\text{-}S)}{T}$	$(T\text{-}S)$	T	$\frac{100(T\text{-}S)}{T}$	(1)/(4)	(1)/(7)
	mgm. E. per cent	*mgm. E. per cent*	*per cent*	*mgm. E. per cent*	*mgm. E. per cent*	*per cent*	*mgm. E. per cent*	*mgm. E. per cent*	*per cent*		
F	10.57	13.03	81.1	3.43	5.89	58.2	4.25	6.71	63.3	3.1	2.5
G	47.23	55.16	85.6	17.57	25.50	68.9	23.00	30.93	74.4	2.7	2.1
B	49.29	60.54	81.4	19.25	30.50	63.1	26.39	37.64	70.1	2.6	1.9
Mean										2.8	2.2

The values obtained by the method of Hissink for the saturation deficits of

the three soils examined are approximately three times those given by a 2-liter extraction with normal sodium chloride solution, and twice those given by a 5-liter extraction. These results are similar in nature to those of von 'Sigmond (32), who considers that by the method of Hissink an overestimate of the value for $(T - S)$ is obtained. Gericke (13) has shown that the procedure of Hissink gives higher values for saturation capacity than that of Gehring (11) and of Bobko and Askinasi (2).

It will be recollected that in the soil of type F, which is of low saturation capacity, replacement of the ionizable hydrogen by the leaching process appears practically complete when five liters of filtrate are obtained. There is no indication that the value for saturation capacity would increase appreciably in magnitude if leaching were continued indefinitely. In the case of this particular soil, therefore, there is strong evidence that reactions other than those of pure exchange occur in the procedure adopted by Hissink. With the heavier soils of types G and B the evidence is less definite, their saturation capacity values show no marked signs of approaching a maximum value at the 5-liter stage of extraction (table 2). Assuming, however, that further leaching would continue to replace 1.57 and 2.14 mgm. E. of hydrogen per liter (the mean of the amounts removed by the fourth and fifth liters from the soils of types G and B, respectively), a total of 16 and 20 liters of filtrate would be necessary to attain the Hissink values.

pH VALUE

The pH values of the soils examined lie between 4.48 and 7.87. The minimum value recorded for the good soils is pH 5.69, and the maximum value for the poor soils, 6.87. The transition soils possess values which range from pH 5.31 to 6.89. The transition and poor soils are, in general, much more acidic in reaction than the medium aged and old soils, respectively, of Holland (table 7). Hissink (17) found that Dutch soils are frequently alkaline in reaction even though their degree of unsaturation is relatively high.

It is to be expected that the ratio of ionizable hydrogen to ionizable calcium present in the soil will exert some measure of control over its hydrogen-ion concentration when in equilibrium with water. The data accumulated uphold this view, in that there is a general tendency for the pH values of the soils of each type to decrease with an increasing degree of unsaturation. The frequent and striking irregularities which occur, however, both for soils within a single type which exhibit a gradation in unsaturation, and for soils of different types with approximately equal degrees of unsaturation, indicate that other factors of primary importance contribute to the determination of pH value. In consequence, the good, transition, and poor soils are not well defined by their hydrogen-ion concentration. The influence of the degree of unsaturation is nevertheless to some extent predominant, for none of the soils in good condition possess pH values which lie at the very acid end of the scale (pH 4.0 to 5.5), and although an appreciable proportion of the poor soils have values

above pH 6.0, none are actually alkaline in reaction. Further, none of the transition soils possess the extreme values pH 4.0 to 5.0 and pH 7.0 to 8.0.

The content of organic matter of the soil is known to be one of the more important of the disturbing factors which affect pH value. Its action has previously been noted by Hissink (17) and other workers, who attribute to the humus present the abnormally high acidity of soils possessing a relatively low degree of unsaturation with calcium. The data obtained for the soils of the cane-growing regions of Trinidad lead to a similar conclusion. The pH values of two series of soils, selected from those examined because the saturation capacity and degree of unsaturation of the soils of each set are approximately constant, are given in table 9. In both series a marked increase in hydrogen-ion concentration occurs as the proportion of organic matter increases. The

TABLE 9

Effect of organic matter content on pH value

SOIL NUMBER	ORGANIC MATTER	SATURATION CAPACITY (CaO PER CENT)	DEGREE OF UNSATURATION	pH VALUE
	per cent		*per cent*	
		Series I		
WOA. 320	1.25	0.525	42.7	6.41
CPD. 3	2.85	0.562	45.0	6.30
M. 27	4.89	0.579	44.7	5.79
M. 151/152	5.32	0.545	43.7	5.20
		Series II		
WOA. 339	1.00	0.539	53.4	6.14
M. 38	3.46	0.553	55.7	5.32
WOPD. 5	4.80	0.537	58.7	4.91

pH value of the soil, therefore, cannot be regarded as a reliable index for soil classification on the basis of field behavior.

PART III.—DETERMINATION OF LIME REQUIREMENT ON THE BASIS OF DEGREE OF UNSATURATION

FACTORS CONTRIBUTING TO THE NEED OF THE SOIL FOR LIME

The ultimate aim of liming is to render the soil more suited to the development in the crop of some particular character or potentiality, such as an increase in yield, an improvement in quality, or a greater resistance to injury from disease or insect pests. This may be attained in one or more of the following ways: by improving the physical structure of the soil; by reducing its degree of acidity to a given value, and incidentally, rendering unexchangeable the ionizable iron and aluminium it contains; or merely by increasing to

a given amount the calcium available to the plant. It is improbable that all crops, and possibly even the same crop under different climatic conditions, will react equally well to any given soil treatment. Further, it is unlikely that each of the three possible courses of action will require an equal amount of lime. It is necessary, therefore, to determine which is most suited to the crop under consideration, under the particular set of conditions which prevail, although the conclusions reached may be of wider application.

Sugar canes in Trinidad, under normal circumstances grow almost equally well on the majority of soils examined, provided that due care is taken in selecting the variety most suited to local conditions, and that the soil is suitably tilled and drained and contains at least 0.2 per cent exchangeable calcium (35). Sugar canes as a class are therefore very tolerant of considerable variation in the physical characteristics of the soil, in its state of unsaturation and degree of acidity. As in the case of other crops (1, 4, 18, 20) it is under adverse circumstances, such as extended periods of meager rainfall or serious infestations of insect pests, that among them marked differences in behavior appear. Then the canes grown on the soils classified in group III are liable to a severe setback, and those on the soils of group II to slight injury, whereas the canes on the soils of group I as a rule remain practically unscathed. Field observations and the data accumulated in the laboratory indicate that it is by their field behavior, rather than by their degree of acidity or their content of exchangeable calcium, that the soils of the three groups are essentially differentiated. In this particular case, therefore, it is primarily to amend their physical condition that the soils of groups II and III appear to need lime.

Under circumstances such as these the manner in which the good soils are differentiated from the others by their degree of unsaturation becomes of practical importance, for once the content of exchangeable calcium and the saturation capacity of a soil are known, it is a matter of simple calculation to determine the lime required to bring its degree of unsaturation within the zone which characterizes the good soils.

FACTORS DETERMINING THE DEGREE OF UNSATURATION OF THE SOILS IN GOOD CONDITION

Equilibrium position of the system soil-calcium carbonate

In addition to the dissimilarity in their degree of unsaturation, the soils in good and poor condition differ outstandingly in that the good soils have been in contact with calcium carbonate for a long period of years. The soils of types D and E of group I are naturally calcareous, whereas those of types C, G, and H, which are classified in this group, have been liberally limed in the past. All these soils, excluding M 40, the store of calcium carbonate of which has but very recently become exhausted, still possess a reserve of limestone. The soils of type E, and those of type D in good condition, with this one possible exception, are undoubtedly in equilibrium with this substance, as in all

probability are the other soils of group I. Such soils were believed by Ramann (31) and Gedroiz (10) to be saturated with calcium, and they are still so considered by some workers (24). Nevertheless, as the data in table 3 demonstrate, they contain exchangeable hydrogen.

The presence of ionizable hydrogen under these conditions is to be expected on theoretical grounds. The compounds formed by the action of calcium carbonate on the acidoid material of the soil are salts of a relatively strong positive ion and a very weak colloidal negative ion, and as such they are prone to hydrolysis. Should the reaction go to completion the normal salt so formed would be unstable, and interaction between it and the hydrogen ions of the soil water would occur. The latter process would result in the formation of unionized (but ionizable) soil acid, and this would proceed until equilibrium conditions were attained.

It appears from these considerations that the saturation deficits of the good soils are measures of the extent to which hydrolysis can occur in them when they are in equilibrium with calcium carbonate, although, as the estimation procedure used does not completely displace the ionizable hydrogen present, the values obtained somewhat underestimate its scope. Similarly their degree of unsaturation is a measure of the proportion of acidoid material unneutralized under these conditions.

These conclusions clarify the meaning of the data obtained. They demonstrate that the amount of lime required completely to neutralize the acidoid material of the soil is in excess of that with which it can normally combine. They show that the degree of unsaturation of the good soils is a measure of the amount of calcium with which they can stably unite, rather than a measure of the point at which the ratio of exchangeable calcium to exchangeable hydrogen is such that the calcium ion exerts a predominating influence over the properties of the soil, although in the good soils such a state of affairs may exist. Further, they indicate that estimations of lime requirements on the basis of the degree of unsaturation of the good soils are essentially determinations of the amounts of lime necessary to bring the soil into equilibrium with calcium carbonate.

Variation in equilibrium position with the soil

The limiting values found for the degree of unsaturation of the good soils (12 and 28 per cent) suggest that a considerable degree of variation with the soil occurs in the proportion of hydrolyzed material present under equilibrium conditions. The data in table 1 demonstrate that the difference between the maximum and minimum values obtained lie well outside the range of experimental error.

$$\underset{\text{(88–72 per cent)}}{[\text{Soil}]\ x\text{Ca}^{\cdot\cdot} + 2x\text{H}^{\cdot}} \rightleftharpoons \underset{\text{(12–28 per cent)}}{[\text{Soil}]\ 2x\text{H}^{\cdot} + x\text{Ca}^{\cdot\cdot}}$$

The deviations from a constant value may be attributed to one or more of the following factors:

First, the presence in the soil of calcium carbonate, which will to some extent pass into solution during the determination of exchangeable calcium, and thus affect the value for the degree of unsaturation.

In selecting samples of the good soils for examination, those with the smallest contents of calcium carbonate were chosen, to reduce this error to a minimum. In consequence, with few exceptions, the amounts present in the soils classified in table 3 are too small appreciably to influence the values obtained.

Secondly, variation in the strength of the acidoid material, both inorganic and organic, with soil type.

Evidence has previously been obtained that under comparable conditions the acidoid complex varies in the extent to which it ionizes in soils of different types (34). A similar variation is shown by the values for the degree of unsaturation of the types of group I. The mean degrees of unsaturation of the soils, which appear to be in equilibrium with calcium carbonate, of types C, E, G, and H, are 21, 22, 26, and 15 per cent, respectively. The difference between the mean values for types G and H is 11 per cent, its standard error being 4.3 per cent. This difference is therefore significant. A fuller exploration of the cause and range of variation within each type is needed, however, before the meaning of such a difference can be accurately assessed.

Thirdly, lack of consistency in the soil content of humified organic matter.

This may be an important factor contributing to the differences found, but insufficient data have been accumulated for an estimation of its effect.

NET AMOUNT OF LIME REQUIRED FOR ATTAINMENT OF EQUILIBRIUM WITH CALCIUM CARBONATE

For reference, table 10 gives the net amounts of lime required to bring into equilibrium with calcium carbonate soils with saturation capacities that range from 0.1 to 1.0 per cent CaO, and with degrees of unsaturation that vary from 20 to 100 per cent. The calculations are based on three assumptions: first, that the degree of unsaturation corresponding to the equilibrium position is 20 per cent, a value which closely approximates to the mean for the soils of group I; secondly, that no loss of lime occurs through soil wash or leaching in the period during which it is reacting with the soil; and thirdly, that an acre-foot of soil weighs 4,000,000 pounds. The examples recorded are classified in accordance with the field behavior of the soils.

When account is taken of the saturation capacity and state of unsaturation of the examples recorded in table 10, the amounts of lime required for the attainment of a state of equilibrium do not appear excessive in magnitude. In rather more than one-half of the cases cited they are less than 5 tons an acre. They exceed 10 tons only when the saturation capacity of the soil reaches a value of 0.4 per cent CaO, and then only when the degree of unsaturation is relatively high. Quantities larger than 20 tons are needed only if a saturation capacity of 0.8 per cent, or more, coexists with a degree of unsaturation greater than 80 per cent. Soils more than 70 per cent unsaturated are uncommon in the cane-growing areas of Trinidad, in spite of the heavy tropical

rainfall and the exhaustive methods of cultivation which have been practiced for generations (36). They are probably of even less frequent occurrence in temperate zones. According to the data in table 10, therefore, in the great majority of cases the amount of lime needed is restricted to a maximum of 16 tons of calcium carbonate to the acre, unless the saturation capacity of the soil exceeds 1 per cent CaO. Of the 50 samples for which data are given in tables 3, 4, and 5, 29 possess requirements less than 5 tons an acre, 14 from 5 to 10 tons, and 7 from 10 to 13 tons.

This method for determining net lime requirement is independent of the presence of calcium carbonate in soils not in equilibrium with calcium carbonate. In such cases the value found for the degree of unsaturation will lie within the zone of unsaturation of the soils of group I only if the amounts

TABLE 10

Net amounts of lime, in tons $CaCO_3$ per acre, required to bring the soil into equilibrium with calcium carbonate

SATURATION CAPACITY (PER CENT CaO)	GOOD SOILS	TRANSITION SOILS		SOILS IN POOR CONDITION						
	Degree of unsaturation (per cent)									
	20	30	35	40	50	60	70	80	90	100
0.10	0	0.32	0.48	0.64	0.96	1.28	1.59	1.91	2.23	2.55
0.20	0	0.64	0.96	1.28	1.91	2.55	3.19	3.83	4.46	5.10
0.30	0	0.96	1.44	1.91	2.87	3.83	4.78	5.74	6.69	7.65
0.40	0	1.28	1.92	2.55	3.83	5.10	6.38	7.65	8.93	10.20
0.50	0	1.59	2.39	3.19	4.78	6.38	7.97	9.56	11.16	12.75
0.60	0	1.91	2.87	3.83	5.74	7.65	9.56	11.48	13.39	15.30
0.70	0	2.23	3.35	4.46	6.69	8.93	11.16	13.39	16.62	17.85
0.80	0	2.55	3.83	5.10	7.65	10.20	12.75	15.30	17.85	20.40
0.90	0	2.87	4.31	5.74	8.61	11.48	14.35	17.22	20.08	22.95
1.00	0	3.19	4.78	6.38	9.56	12.75	15.94	19.13	22.32	25.50

present are in excess of those necessary for the attainment of a state of equilibrium. If present in quantities smaller than this, the additional quantities required can be calculated in the normal manner from the apparent degree of unsaturation found.

NEED FOR A RESERVE OF CALCIUM CARBONATE IN THE SOIL

Repression of ionization

The fact that the degree of unsaturation of the soils in good condition appears to be a measure of the equilibrium position of the system soil-calcium carbonate, rather than an indication of the point at which the soil content of exchangeable calcium is large enough to impress the characteristics of a calcium

clay upon the soil, renders it doubtful whether differences in the degree of unsaturation alone, always afford a complete explanation of the dissimilarity in the behavior of the soils examined, and suggests that the calcium carbonate of itself may, under certain conditions, play an important part. The relatively small differences in the degree of unsaturation of the soils of groups I and II, in comparison with the contrast displayed by their properties, tend to confirm this possibility. It seems likely, in the case of the soils of group I, that the calcium ions, to which the calcium carbonate gives rise, suppress in large measure the ionization of the calcium salts of the acidoid material of the soil, thereby acting as a coagulating agent. In the soils of group II (and those of group III) ionization can occur unhindered, and this may contribute materially to the deterioration evident in their physical structure. The action of the ions derived from the calcium carbonate would thus be akin to the repression of the ionization of an ordinary electrolyte, by the mass influence of an added ion common to both electrolytes.

Maintenance of the degree of unsaturation at equilibrium value

It has been pointed out by Hissink (17) that the soils of Holland of medium age differ but little in their degree of unsaturation from those newly endyked (table 7). Both series of soils contain calcium carbonate, but the amounts present in those of medium age are much the smaller. This substance is absent from the old and very old soils, which tend to be much more highly unsaturated than the soils of the other groups. Hissink concludes that calcium is lost through leaching originally at the expense of calcium carbonate present, and that when it is exhausted, losses of exchangeable calcium from the clay material begin. The data recorded in tables 3, 4, and 5 lead to a similar conclusion. They indicate that the degree of unsaturation of the soils of group I is maintained by their store of calcium carbonate at a value which approximates 20 per cent, and that it is not until the store is consumed that the degree of unsaturation commences appreciably to increase.

It is probable that the calcium removed from the soil by leaching is initially present in solution either as unionized calcium bicarbonate or in the form of ions. The ions are probably derived chiefly from the dissolved calcium salt of the relatively strong bicarbonate ion, rather than from the very slightly ionized salts of the weakly acidic clay complex. If the state of equilibrium in the soil solution is displaced through loss under these circumstances, it would be restored almost entirely by further ionization of the calcium bicarbonate. which in turn would be replaced by solution of the calcium carbonate present,

It appears advisable, therefore, both from the point of view of repression of ionization and the maintenance of the soil content of exchangeable calcium, to make provision in estimates of lime requirement for amounts of calcium carbonate in excess of those necessary for the creation of equilibrium conditions. The excess included for the purpose of forming a reserve must necessarily be

TABLE 11

Comparison of net lime requirements as determined by (a) pH value method of Hardy and Lewis and (b) method of degree of unsaturation

SOIL TYPE	SOIL NUMBER	TONS $CaCO_3$ REQUIRED TO BRING		RATIO B/A
		(A) pH to 7.0*	(B) Degree of unsaturation to 20 per cent	
		Group I. Soils in good condition		
C	M. 64	1.08	0.00	0
C	M. 101	0.54	0.41	0.76
D	M. 181	1.08	0.00	0
E	MPD. 7	0.93	0.03	0.03
G	CA. 15	1.31	0.61	0.47
G	CPD. 1	0.41	0.86	2.10
G	CA. 16	0.67	1.05	1.57
H	O. 59	2.74	0.00	0
H	A. 10	0.80	0.00	0
Mean value				0.55
		Group II. Transition soils		
C	M. 71	2.55	2.30	0.90
G	W. 48	1.40	2.74	1.96
H	O. 122	2.04	1.05	0.51
Mean value				1.12
		Group III. Soils in poor condition		
A	M. 50	4.40	7.37	1.68
B	MPD. 9	6.63	10.36	1.56
G	W. 62	2.46	4.34	1.76
G	CPD. 3	2.74	4.50	1.64
G	CA. 2	10.00	9.82	0.98
G	W. 106	9.57	8.23	0.86
G	WOA. 341	1.66	2.62	1.58
G	WOPD. 5	8.71	6.63	0.76
G	CA. 1	11.16	13.01	1.17
G	WOPD. 3	8.61	10.81	1.26
H	WOA. 320	3.25	3.79	1.17
H	WOA. 339	3.51	5.74	1.64
H	WOA. 332	4.82	6.60	1.37
Mean value				1.34

* The lime requirements in this column were calculated from data provided by Prof. F. Hardy.

greater than losses due to the action of rain water over the period during which the soil content of exchangeable calcium is being increased to its maximum value. In Great Britain these losses are estimated to amount to half a ton an acre (26). In the humid tropics they are undoubtedly larger, but their actual magnitude is as yet unknown.

COMPARISON WITH RESULTS OBTAINED BY THE pH VALUE METHOD OF HARDY AND LEWIS

Hardy and Lewis (14) have devised a method for determining the amount of lime required to reduce the acidity of soils to a pH value of 7.0. According to their procedure 10 gm. of soil is mixed with 40 cc. of neutral 0.2 N $CaCl_2$ solution and titrated with 0.03 N $Ca(OH)_2$, which is added in successive portions of 5 cc. at 3-minute intervals with shaking. The pH value is determined after each addition by means of the quinhydrone electrode, and the titration is continued until an alkaline reaction is obtained. The results are plotted in the form of a graph, from which the amount of calcium hydroxide, and hence calcium carbonate, required to give a pH value of 7.0 is read. For the purpose of comparison, table 11 records the net lime requirements of a selected series of soils, as determined by the method of unsaturation and by the alternative method of pH value of Hardy and Lewis.

The data in this table indicate that:

The net lime requirements of the soils of group I are larger when determined by the method of Hardy and Lewis than by the method of unsaturation. This may be explained on the grounds that although these soils are in equilibrium with calcium carbonate, they still contain readily exchangeable hydrogen, which is in part replaced by the treatment with calcium chloride and calcium hydroxide.

The net lime requirements of the soils of group III, on the other hand, as a rule are considerably smaller when determined according to the pH value method than according to the method of unsaturation. This suggests that the amount of hydrogen replaced by the former method from soils in a condition of relatively high unsaturation is in general less than that required to reduce their degree of unsaturation to 20 per cent.

The lime requirements as given by the two methods for the 16 soils of groups II and III are highly correlated, r being equal to $+0.911$, with P less than 0.01.

SUMMARY

There is considerable evidence that hydrogen and calcium together account for the great majority of the exchangeable ions present in the soils of humid climates. Upon the relative proportions in which these ions occur, and possibly also on their absolute amounts, the properties of such soils may be expected to depend. An investigation has therefore been made of the extent to which the calcium-hydrogen status of a series of soils is related to their field behavior, and upon the conclusions reached a method for determining lime requirement has been based.

1. Exchangeable calcium and hydrogen together (saturation capacity) were determined by leaching to two liters according to the modified method of Page and Williams. Exchangeable calcium was measured by the method of Hissink, and exchangeable hydrogen (saturation deficit) determined by difference. From these data the degree of unsaturation was calculated.

A critical study of the procedure used has shown that:

The mean values obtained for saturation capacity, exchangeable calcium, saturation deficit, and degree of unsaturation, from duplicate estimations on a single subsample, give a sufficiently close approximation to those obtained from the examination of a number of subsamples for most purposes of soil differentiation and characterization.

Only partial replacement results from leaching to two liters. Measurements of the degree of unsaturation based on a 2-liter (or possibly even a 1-liter) extraction may nevertheless be used with a fair degree of confidence in comparative studies of soils, for, (*a*) constant results are obtained on repetition for the amounts of calcium and hydrogen removed, (*b*) the ratios of the values for degree of unsaturation, determined on the basis of 1-, 2-, 3-, and 4-liter extractions, to those given by a 5-liter extraction, closely approximate constants, apparently independent of the type and saturation capacity of the soil, and (*c*) exchange of hydrogen occurs to such an extent that the ratios of replaced hydrogen to calcium in good and poor soils are sufficiently different adequately to reflect the dissimilarity in their properties.

In the case of saturation capacity and saturation deficit the ratios of the values given by 2-liter and 5-liter extractions decrease significantly with increasing saturation capacity. . The measurements obtained for saturation capacity and saturation deficit may therefore not be strictly comparable.

II. The samples taken from the eight soil types examined were classified into three groups:

Group I. Soils possessing an inherent good tilth
Group II. Soils in the transition stage from group I to group III
Group III. Soils possessing a badly impaired physical condition

The data obtained have demonstrated that:

1. No regular relationship exists between field behavior and magnitude of saturation capacity provided it is greater than 0.25 per cent CaO.

2. The relationship between field behavior and the content of exchangeable calcium and the saturation deficit of the soil is markedly evident only in types of fairly uniform saturation capacity.

3. The soils of groups I, II, and III each lie within fairly well-defined zones of unsaturation.

Group I. 12 to 28 per cent, with a mean value of 21 per cent
Group II. 30 to 35 per cent, with a mean value of 32 per cent
Group III. Greater than 38 per cent

The delimiting values of the three zones appear independent of: the nature of the colloidal material of the soils examined; the degree of colloidality of the soil; any variation which may occur in the soil content of exchangeable ions other than calcium or hydrogen; the agricultural history of the soils.

The degree of unsaturation therefore appears to be a master factor controlling the field behavior of the soil. The relatively small amounts of organic matter present in the soils examined may aid in emphasizing its importance in this respect.

4. A general tendency exists for the pH value of the soil to decrease with increasing un-

saturation, but frequent and striking irregularities occur which indicate that other factors of primary importance contribute to the determination of pH value. In consequence, the soils of groups I, II, and III are not well defined by their hydrogen-ion concentration. The soil content of organic matter appears to be an important disturbing factor.

5. The modified procedure of Page and Williams gives much lower values than the titrimetric method of Hissink for the degree of unsaturation. A comparison of the values given by the two processes for a soil of low saturation capacity has afforded clear evidence that with the Hissink method reactions other than those of pure exchange occur.

III. Evidence is adduced that the soils of group I are in equilibrium with calcium carbonate. If such is the case, the saturation deficits of these soils are measures of the extent to which hydrolysis can occur, and the degree of unsaturation is a measure of the proportion of the acidoid material hydrolyzed under these conditions. This suggests that the degree of unsaturation of the good soils is a measure of the amount of calcium with which they can stably unite, rather than an indication of the point at which the ratio of exchangeable calcium to hydrogen is such that the former ion exerts a predominating influence over the properties of the soil, although in the good soils such a state of affairs may exist.

The limiting values found for the degree of unsaturation of the good soils (12 and 28 per cent) indicates that a considerable degree of variation with the soil occurs in the proportion of hydrolyzed material present under equilibrium conditions. This is probably due to variation in the strength of the acidoid material from soil to soil, a factor which may be influenced by the soil content and nature of humified organic matter.

A table has been given of the net amounts of calcium carbonate required to reduce to 20 per cent the degree of unsaturation of soils of varying saturation capacities and degrees of unsaturation.

Attention has been drawn to the need for maintaining a reserve of calcium carbonate in the soil, both for the purpose of repressing the ionization of the calcium salts of the acidoid material, and of preserving the degree of unsaturation at a value approximating to 20 per cent.

A comparison has been made of the lime requirements of a series of soils as determined by the method of unsaturation and the pH value method of Hardy and Lewis.

REFERENCES

(1) Andrews, E. A. (n.d.) Factors Affecting the Control of the Tea Mosquito Bug (*Helopeltis theivora*–Waterh.). Indian Tea Association, London.

(2) Bobko, B. W., and Askinasi, D. L. 1925 Die Methode zur Bestimmung der Absorptionskapazität. *Ztschr. Pflanzenernähr. u. Düngung* (A) 4: 103.

(3) Bradfield, R. 1924 The importance of hydrogen-ion concentration control in physico-chemical studies of heavy soils. *Soil Sci.* 17: 411.

(4) Comber, N. M. 1925 Discussion on base exchange in soils. *Faraday Soc. Trans.* 20: 613.

(5) Cummins, A. B., and Kelley, W. P. 1923 The formation of sodium carbonate in soils. Calif. Agr. Exp. Sta. Tech. Paper 3.

(6) FISHER, R. A. 1928 Statistical Methods for Research Workers. London.
(7) GEDROIZ, K. K. 1914 Colloid chemistry as related to soil science: II. Rapidity of reaction exchange in the soil. The colloidal condition of the soil saturated with various bases. The indicator method of determining the colloidal content of the soil. *Zhur. Opytn. Agron.* (Russian) 15: 181.
(8) GEDROIZ, K. K. 1916 The absorbing capacity of the soil and the zeolitic bases of the soil. *Zhur. Opytn. Agron.* (Russian) 17: 472.
(9) GEDROIZ, K. K. 1922 On the Absorptive Power of Soils. Publ. of the Editorial Committee of the People's Commissariat of Agriculture, Petrograd.
(10) GEDROIZ, K. K. 1924 Soils unsaturated with bases. A method of determining in soils the hydrogen present in an absorbed condition. Soil requirement of lime as a neutralizing agent. *Zhur. Opytn. Agron.* (Russian) 22: 3.
(11) GEHRING, A., PEGGAU, A., AND WEHRMANN, O. 1926 Untersuchungen über die Feststellung des Kalkbedürfnisses Braunschweigischer Böden. *Trans. Second Comm. Internatl. Soc. Soil Sci.* A: 153.
(12) GEHRING, A., PEGGAU, A., AND WEHRMANN, O. 1927 Über die Methode zur Bestimmung des Kalkbedürfnisses des Bodens unter Benutzung des Sättigungszustandes an Kalk. *Ztschr. Pflanzenernähr. u. Düngung.* (A) 8:321.
(13) GERICKE, S. 1927 Vergleichende Untersuchungen über Bestimmungs-methoden des Sättigungszustandes des Bodens. *Ztschr. Pflanzenernähr. u. Düngung.* (A) 9: 20.
(14) HARDY, F., AND LEWIS, A. H. 1929 A rapid electrometric method for measuring "lime requirements" of soils. *Jour. Agr. Sci.* 19: 17.
(15) HARDY, F. 1929 The soils of Trinidad sugar estates. The distribution of textural types: I. Soils of the Central Plain. *Minutes and Proc. of the Froghopper Invest. Com. Trinidad* 15: 243.
(16) HISSINK, D. J. 1922 Beitrag zur Kenntnis der Adsorptions-vorgänge im Boden. *Internatl. Mitt. Bodenk.* 12: 81.
(17) HISSINK, D. J. 1925 Base exchange in soils. *Faraday Soc. Trans.* 20: 551.
(18) HISSINK, D. J. 1925 Discussion on base exchange in soils. *Faraday Soc. Trans.* 20: 612.
(19) HISSINK, D. J. 1925 Der Sättigungszustand des Bodens. A. Mineralböden (Tonböden). *Ztschr. Pflanzenernähr u. Düngung* (A) 4: 137.
(20) HUTCHINSON, H. B. 1925 Discussion on base exchange in soils. *Faraday Soc. Trans.* 20: 613.
(21) JOFFE, J. S., AND MCLEAN, H. C. 1926 Colloidal behavior of soils and soil fertility. II: The soil complex capable of base exchange and soil acidity. *Soil Sci.* 21: 181.
(22) JOFFE, J. S., AND MCLEAN, H. C. 1927 Colloidal behavior of soils and soil fertility. III. Cation replacement and saturation of soil with Ca. *Soil Sci.* 23: 127.
(23) KELLEY, W. P., AND BROWN, S. M. 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.
(24) KELLEY, W. P., AND BROWN, S. M. 1927 Base unsaturation in soils. *Proc. First Internatl. Cong. Soil Sci.* 2: 491.
(25) MCLEAN, W., AND ROBINSON, G. W. 1924 A new method for the determination of ammoniacal nitrogen in soils. *Jour. Agr. Sci.* 14: 548.
(26) Ministry of Agriculture (London), 1927 The use of lime in agriculture. Leaflet 170.
(27) OGG, W. G., AND DOW, W. T. 1928 The reaction, exchangeable calcium, and "lime requirement" of certain Scottish soils. *Jour. Agr. Sci.* 18: 131.
(28) OSUGI, S., AND SANO, Y. 1927 Degree of saturation and the absorbed bases of Japanese soils. *Bul. Agr. Chem., Soc. Japan.* 3: 71.
(29) PAGE, H. J., AND WILLIAMS, W. 1925 Studies on base exchange in Rothamsted soils. *Faraday Soc. Trans.* 20: 573.
(30) PAGE, H. J., AND WILLIAMS, W. 1926 The effect of flooding with sea water on the fertility of the soil. *Jour. Agr. Sci.* 16: 551.

(31) RAMANN, E. 1911 Bödenkunde. Berlin.
(32) VON' SIGMOND, A. A. J. 1926 Einige Vergleichende Untersuchungen über die Bestimmung der Austauschfähigen Kationen, Sättigungszustand und Aziditätsverhältnisse im Boden. *Trans. Second Comn. Internatl. Soc. Soil. Sci* A: 55.
(33) SMITH, A. M. 1925 The exchangeable bases in some Scottish Soils. *Jour. Agr. Sci.* 15: 466.
(34) TURNER, P. E. 1928 An investigation of the method of Page and Williams for the determination of the saturation capacity of soils. *Jour. Agr. Sci.* 18: 257.
(35) TURNER, P. E. 1929 The lime status of soil in relation to an insect pest of sugar cane. *Jour. Agr. Sci.* 19: 26.
(36) TURNER, P. E. 1929 Liming as a factor in the amelioration of deteriorated tropical soils. *Jour. Agr. Sci.* 19: 83.
(37) WILLIAMS, R. 1928 The determination of exchangeable calcium in carbonate-free soils. *Jour. Agr. Sci.* 18: 439.

THE DECOMPOSITION OF LIGNIFIED MATERIALS BY SOIL MICROÖRGANISMS

MAX. PHILLIPS, HERMAN D. WEIHE, AND N. R. SMITH[1]

U. S. Department of Agriculture

Received for publication March 8, 1930

In examining the literature on the subject of the decomposition of lignin or lignified tissues by means of microörganisms, one gets the impression that lignin, either in the free state or in the chemical form found in various lignified plant tissues, is comparatively resistant to the action of microörganisms. The present investigation was undertaken to determine whether lignin as it occurs in plant materials can be decomposed by the microörganisms found in the soil.

Rose and Lisse (9) made a chemical examination of a sound sample of Douglas fir heart, also of one partly rotted, and of one almost completely rotted. They found that the percentage of cellulose and pentosans decreased with the advance in the decomposition of the wood, whereas the alkali-soluble fraction and the percentage of methoxyl increased. They conclude from their results that lignin is far more resistant to decomposition than cellulose, although no direct determinations of lignin were made.

Schrader (10) found that bacteria were incapable of breaking down lignin prepared by the Willstätter method, at least in the experimental period of 25 days.

Pringsheim and Fuchs (8), after adding the necessary inorganic salts, inoculated alkali lignin with forest soil. The product obtained differed from the original material in containing up to one-half of its weight of substances soluble in alcohol, although the original lignin was practically insoluble in alcohol. The alcohol-soluble fraction was found to have a smaller percentage of methoxyl but a greater percentage of carbon than the original lignin. The fraction insoluble in alcohol showed some decrease in percentage methoxyl, but the percentage carbon was not affected.

Bray and Andrews (2) and du Toit (14), studying the decomposition of wood with pure cultures of fungi and molds, found that the cellulose was rapidly decomposed, whereas the lignin remained practically intact.

Smith (13), in studying the chemical changes in apple wood brought about by decay due to *Polystictus versicolor* Fr., found that the percentage lignin was greater in the sample of decayed wood than in the sound wood. The absolute quantity of lignin present in each case was not determined directly. Using an indirect method, however, Smith obtains data which show that the lignin was practically unattacked.

Waksman (15) found that the lignins are more resistant to the action of fungi and bacteria than any of the other major ingredients of natural organic materials. The accumulation of lignin in the soil is believed by Waksman to account for a large part of soil humus.

Waksman and Tenney (16, p. 405) as a result of their studies on the decomposition of various plant materials conclude that, "Lignins are not decomposed in the soil, at least within the

[1] The two first-named authors are senior chemist and junior chemist, respectively, Color and Farm Waste Division, and the last-named author is senior bacteriologist, Division of Soil Microbiology, Bureau of Chemistry and Soils.

experimental period of 32 to 35 days. If they are decomposed at all, the amount of decomposition is only insignificant in comparison with the decomposition of the other constituents of natural organic matter."

Marcusson (7) determined the Cross and Beven cellulose and lignin in sound wood, in partly decayed wood, and in completely decayed wood. He found that when the material was first extracted on the water bath for 1 hour with 1 per cent sodium hydroxide solution and lignin determinations (fuming hydrochloric acid method) were made on this partly purified product, the percentage of lignin was about the same in all cases. The increase in alkali-soluble substances found by Rose and Lisse (9) in decayed wood was shown to be due to a degradation product of the cellulose. Waksman and Stevens (19) have shown, however, that the method used by Marcusson for the determination of lignin gives too low results because of partial removal of the lignin by the alkali.

Falck and Haag (4) conclude from their studies that in the microbiological decomposition of plant materials two distinct processes take place, namely, "destruction" and "corrosion." The effect of "destruction" is to decompose the cellulose and pentosans, the lignin being very little affected. "Corrosion" on the other hand causes slow decomposition of both lignin and cellulose.

Schwalbe and Ekenstam (11) examined pine wood which had been rotted by *Merulius lachrymans* and found the percentage of lignin very high, 73 per cent, whereas the percentage of cellulose was only 15 per cent. No pentosans were found. The lignin isolated from the rotted material by the Willstätter method was found to have a lower methoxyl content than that obtained by the same method from sound wood.

Waksman and Tenney (17, 18) studied the decomposition of the rye plant by soil microorganisms, as well as that of rye straw, cornstalks, and alfalfa tops. They found that the lignin decomposed less rapidly than any of the major plant constituents and conclude that (17, p. 332), "The accumulation of the lignins, which resist decomposition more than the other plant constituents, and the synthesis of microbial nitrogenous complexes account for the increase in soil 'humus' as a result of decomposition of natural organic materials."

EXPERIMENTAL METHOD

In the experiments here reported four typical lignified plant materials were used; namely, cornstalks, oat hulls, corncobs, and wheat straw. The materials were dried at 105° C. and the following determinations were made:

Pentosans were determined by Tollens' method. The directions given in the Book of Methods of the Association of Official Agricultural Chemists for carrying out this determination were followed (1).

Cellulose was determined by the Sieber and Walter (12) modification of the Cross and Bevan method. Instead of Gooch crucibles, prepared as recommended by Sieber and Walter, Jena sintered glass crucibles were used.

Lignin. The material was finely ground in a mill and the lignin determined by the fuming hydrochloric acid method of Willstätter and Zechmeister (2). The procedure recommended by Dore (3) was followed.

Ash was determined by igniting a weighed sample with a Bunsen burner and weighing the nonvolatile residue.

Methoxyl was determined according to the Kirpal and Bühn (6) modification of the Zeisel (5) method. To the hydriodic acid (10 cc.) 3 cc. phenol was added as recommended by Weishut (20).

Nitrogen was determined by the Kjeldahl method.

The results of the various determinations made on the original plant materials prior to their decomposition by the soil microörganisms are given in table I.

MICROBIOLOGICAL EXPERIMENTS

In order to determine whether the lignin present in cornstalks, oat hulls, corncobs, and wheat straw could be decomposed by the microörganisms of the soil, three series of experiments were conducted. In the first series, 10-gm. samples of the oven-dry (105°C.) materials were used and in the second and third series 25-gm. samples were employed. Czapek's solution was used as the culture medium in the first series of experiments (table 2). At the end of the incubation period of the first series of experiments, it was observed that the pH of the medium was rather high (pH 8.0 to 9.0). In the second and third series of experiments a modified Czapek's solution was accordingly employed. In place of the sodium nitrate an equivalent quantitiy of urea was added. When the modified Czapek's solution was used, the reaction of the medium remained close to neutrality throughout the experiment. The flasks containing the lignified plant materials were all inoculated with the same soil

TABLE 1

Composition of materials used in experiments with soil organisms

(Analysis made on materials dried at 105 °C.)

MATERIAL	PENTOSANS	CELLULOSE (CROSS AND BEVAN)	LIGNIN	ASH	$-OCH_3$	N
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Corn stalks	24.51	52.4	16.75	5.28	2.60	1.08
Oat hulls	37.53	51.5	17.35	6.04	2.49	0.23
Corn cobs	36.18	56.2	23.90	1.47	2.23	0.36
Wheat straw	28.53	56.4	25.70	5.33	2.70	0.40

infusion and incubated at 28°C. The incubation period for the first series of experiments was from October 8 to November 13 (table 2) and for the second and third series, from December 20, 1928, to January 14, 1929, and from December 20, 1928, to February 20, 1929, respectively (tables 3 and 4). At the end of each incubation period the residual lignified material remaining in each flask was filtered off, washed with distilled water, dried at 105°C., and weighed. From the results thus obtained the loss in weight due to the microbiological action was determined. The percentages of pentosans, cellulose, lignin, ash, methoxyl, and nitrogen contained in this dry material were then determined by aforementioned analytical methods. The result of each determination was calculated on the basis of the initial weight of material used. By comparing these results with those obtained in the analysis of the materials in the original state, data were obtained showing the absolute loss of each constituent, brought about by the action of the microörganisms. The results of the first, second, and third series of experiments are recorded in tables 2, 3, and 4, respectively.

TABLE 2

Analytical results showing effect of selective decomposition of lignified materials with soil organisms

(Analyses made on materials dried at 105°C.)

MATERIAL*	WEIGHT AT END OF EXPERIMENT	LOSS IN WEIGHT	PENTOSANS			CELLULOSE (CROSS AND BEVAN)			LIGNIN			ASH			METHOXYL			NITROGEN		
			Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Corn stalks	6.178	38.20	21.4	13.2	46.1	52.0	32.1	38.7	27.07	16.72	0.17	5.14	3.18	39.8	2.95	1.82	30.0	0.96	0.59	45.3
Oat hulls	8.770	12.30	38.4	33.7	10.2	52.5	46.0	10.6	18.72	16.41	5.4	5.55	4.86	19.5	2.71	2.38	4.4	0.16	0.14	39.1
Corn cobs	7.535	24.65	29.7	22.4	38.1	58.8	44.3	21.1	26.32	19.83	17.0	0.74	0.55	62.5	2.67	2.01	9.8	0.47	0.35	2.7
Wheat straw	6.983	30.17	26.5	18.5	35.0	53.1	37.1	34.2	22.15	15.46	39.8	4.52	3.85	27.7	3.78	2.64	2.2	0.46	0.32	20.0

* 10 gm. material used in each experiment. Incubated from October 8 to November 13, 1928.

TABLE 3

Analytical results showing the effect of selective decomposition of lignified materials with soil organisms

(Analyses made on materials dried at 105°C.)

MATERIAL*	WEIGHT AT END OF EXPERIMENT	LOSS IN WEIGHT	PENTOSANS			CELLULOSE (CROSS AND BEVAN)			LIGNIN			ASH			METHOXYL			NITROGEN		
			Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Corn stalks	13.80	44.8	25.54	14.10	40.7	46.9	25.9	50.5	22.46	12.40	25.9	2.27	1.25	76.1	3.35	1.85	28.8	1.20	0.66	38.8
Oat hulls	21.55	13.8	40.90	35.25	6.0	47.7	41.1	20.2	18.50	15.94	8.1	5.23	4.50	25.5	2.74	2.36	5.2	0.28	0.24	0
Corn cobs	19.27	22.9	30.40	23.43	35.2	50.3	38.7	31.1	18.28	14.09	41.0	0.58	0.44	70.0	2.84	2.18	2.2	0.50	0.38	0
Wheat straw	17.07	31.3	28.74	19.62	31.2	52.7	36.0	36.1	19.44	13.27	48.3	4.28	2.92	45.2	3.50	2.39	11.4	0.46	0.31	22.5

* 25 gm. material used in each experiment. Incubated from December 20, 1928, to January 14, 1929.

TABLE 4

Analytical results showing the effect of selective decomposition of lignified materials with soil organisms

(Analyses made on materials dried at 105°C.)

MATERIAL*	WEIGHT AT END OF EXPERIMENT	LOSS IN WEIGHT	PENTOSANS			CELLULOSE (CROSS AND BEVAN)			LIGNIN			ASH			METHOXYL			NITROGEN		
			Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss	Found	Calculated on original weight	Loss or gain
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Corn stalks	12.28	50.9	28.00	13.75	43.9	52.9	26.0	50.3	24.22	11.89	29.0	2.25	1.10	79.1	3.65	1.39	46.5	0.88	0.43	−60.1
Oat hulls	18.89	24.4	42.03	31.75	15.40	44.1	33.3	35.3	20.82	15.73	9.3	6.67	5.04	16.5	2.85	2.15	13.6	0.39	0.29	(+26.0)
Corn cob	15.85	36.6	36.61	23.21	35.8	58.1	36.8	34.5	20.70	13.12	45.1	0.97	0.61	58.5	2.80	1.77	20.6	0.63	0.39	(+7.6)
Wheat straw	13.04	27.8	30.00	19.56	31.44	52.0	33.9	39.9	25.42	16.87	34.3	4.09	2.66	50.0	4.15	2.70	0	0.63	0.41	(+2.5)

* 25 gm. material used for each experiment, except in case of wheat straw where 20 gm. was used. Incubated from December 20, 1928 to February 20, 1929.

DISCUSSION

It will be observed from tables 2, 3, and 4 that in every case a considerable decrease in the quantity of pentosans and cellulose (Cross and Bevan) resulted from the action of the soil microörganisms. The absolute quantity of lignin, as well as the percentage of lignin, showed a decided decrease in nearly all of the experiments. In some of the experiments the loss of lignin, was as great as that of the cellulose and pentosans and in some instances even greater. This indicates conclusively that the soil microörganisms are capable of breaking down the lignin present in lignified plant materials. The greatest loss occurred in those experiments in which urea was used as the source of nitrogen. Whether by prolonged action the microörganisms of the soil are capable of breaking down all the lignin present, or whether a lignin degradation product is finally obtained which resists further decomposition, is not known. The experiments were not continued long enough to answer this question. Moreover, these experiments were conducted largely under aërobic conditions. Under strictly anaërobic conditions it may very well be, as some investigators hold, that the lignin is not decomposed, or at least only to a limited extent.

In all these experiments, except one, the methoxyl content decreased. Methoxyl groups are present in lignin, and with the loss of lignin a decrease in the methoxyl content of the material is to be expected. The authors are, of course, aware of the limitations of the methoxyl determination as applied to such a natural product as straw or cornstalks. That by far the largest percentage of the methoxyl found in lignified plant materials, such as straw, cornstalks, and corncobs, is due to the lignin present may be accepted as reasonably certain. The results on the methoxyl determinations also indicate a loss of lignin.

The fact that soil organisms are apparently capable of breaking down lignin as found in natural lignified plant materials in no way implies, of course, that they are equally capable of decomposing the lignin prepared either by the fuming hydrochloric acid method, by the 72 per cent sulphuric acid method, or by the alkali method. There is no evidence to support the claim that the lignin prepared in the laboratory is identical with the natural substance. The comparatively strong reagents that are employed for the isolation of lignin undoubtedly bring about drastic changes in its composition. It would hardly be expected that the lignin obtained by the hydrochloric, sulfuric, or alkali, methods would be identical with that in the plant substance.

SUMMARY

A study of the selective decomposition by soil microörganisms of the various constituents in cornstalks, oat hulls, corncobs, and wheat straw was made. The results indicate that a rapid decomposition of the pentosans and cellulose (Cross and Bevan) takes place.

Under proper conditions soil organisms are capable of decomposing lignin as found in lignified plant materials. Under suitable conditions the rate of

decomposition of the lignin may be as great as that of the cellulose (Cross and Bevan) and pentosans.

REFERENCES

(1) Association of Official Agricultural Chemists 1925 Official and Tentative Methods of Analyses, Revised to 1925. Washington, D. C.

(2) Bray, M. W., and Andrews, T. M. 1924 Chemical changes of groundwood during decay. *Indus. and Engin. Chem.* 16: 137–139.

(3) Dore, W. H. 1920 The proximate analysis of hardwoods: Studies on *Quercus agrifolia*. *Indus. and Engin. Chem.* 12: 984–987.

(4) Falck, R., and Haag, W. 1927 Der Lignin und der Cellulose—Abbau des Holzes, zwei Vershiedene Zersetzungs Prozesse durch holz-bewohnende Fadenpilze. *Ber. Deut. Chem. Gesell.* 60: 225–232.

(5) Houben, J. 1923 Die Methoden der Organischen Chemie, III.: 144. Georg Thieme, Leipzig.

(6) Kirpal, A., and Bühn, T. 1914 Methoxyl-Bestimmung Schwefelhaltiger Verbindungen. *Ber. Deut. Chem. Gesell.* 46: 1084–1087; also in *Monatsh. Chem.* 36: 853–863 (1915).

(7) Marcusson, J. 1926 Lignin und Oxycellulosetheorie. *Ztschr. Angew. Chem.* 39: 898–900.

(8) Pringsheim, H., and Fuchs, W. 1923 Über den bakteriellen abbau von Lignisäure. *Ber. Deut. Chem. Gesell.* 56: 2095–2097.

(9) Rose, R. E., and Lisse, M. W. 1917 The chemistry of wood decay. Paper I—Introductory. *Jour. Indus. and Engin. Chem.* 9: 284–287.

(10) Schrader, H. 1921 Über das Verhalten von Cellulose, Lignin, Holz, und Torf gegen Bakterien. *Gesam. Abhandl. zur Kenntnis der Kohle* 6: 173–176.

(11) Schwalbe, C., and Ekenstam, A. 1927 Zur Kenntnis des durch Hausschwamm auf Kiefernholz erzeugtes Lignins. *Cellulosechemie* 8: 13–15.

(12) Sieber, Rudolf, and Walter, L. E. 1913 Zellulosebestimmungsmethode für Holz nach dem Verfahren von Cross und Bevan. *Papier Fabrik.* 11: 1179–1183.

(13) Smith, R. G. 1924 A chemical and pathological study of decay of the xylem of the apple caused by *Polystictus versiocolor* Fr. *Phytopathology* 14: 114–118.

(14) Toit, du 1926 The origin and mode of formation of humic matter in the soil. Thesis Cambridge University, 1924. (Cited by Waksman, *Soil Sci.* 22: 144.)

(15) Waksman, S. A. 1926 The origin and nature of the soil organic matter or soil "humus": III. The nature of the substances contributing to the formation of humus. *Soil Sci.* 22: 323–333.

(16) Waksman, S. A., and Tenney, F. G. 1926 On the origin and nature of the soil organic matter or soil "humus": IV. The decomposition of the various ingredients of straw and of alfalfa meal by mixed and pure cultures of microörganisms. *Soil Sci.* 22: 395–406.

(17) Waksman, S. A., and Tenney, F. G. 1927 The composition of natural organic materials and their decomposition in the soil: II. Influence of age of plant upon the rapidity and nature of its decomposition—rye plants. *Soil Sci.* 24: 317–333.

(18) Waksman, S. A., and Tenney, F. G. 1928 Composition of natural organic materials and their decomposition in the soil: III. The influence of nature of plant upon the rapidity of its decomposition. *Soil Science*, 26: 155–171.

(19) Waksman, S. A., and Stevens, K. R. 1929 Processes involved in the decomposition of wood with reference to the chemical composition of fossilized wood. *Jour. Amer. Chem. Soc.* 51: 1187–1196.

(20) Weishut, F. 1912 Methoxyl Bestimmungen mit Phenolhaltiger Jodwasserstoffsäure. *Monatsh. Chem.* 33, 1165–1172.

(21) Willstätter, R., and Zechmeister, L. 1913 Zur Kenntnis der Hydrolyse von Cellulose: I. *Ber. Deut. Chem. Gesell.* 46: 2401–2412.

THE DETERMINATION OF THE REPLACEABLE BASES AND THE BASE-EXCHANGE CAPACITY OF SOILS[1]

H. D. CHAPMAN AND W. P. KELLEY

University of California

Received for publication March 12, 1930

The purpose of this paper is to present a brief discussion of the methods for, and the errors involved in, the determination of replaceable bases in soils; to discuss the results of some special studies on methods for the determination of replaceable bases in soils containing alkaline earth carbonates; and to give the results of special studies on the determination of base-exchange capacity by the NH_4-absorption method.

The determination of the replaceable bases is complicated by the fact that various kinds of soil substances react with salt solutions and dilute acids. As is well known, the reaction which takes place between the base-exchange material and electrolytes is characterized by an exchange of ions, but with various other constituents this is not necessarily the case. Certain minerals that occur more or less widely in soils yield bases to salt solutions probably chiefly as a result of decomposition and ordinary solution processes. For example, finely ground hornblende, biotite, serpentine, and wollastonite are comparatively easily decomposed by neutral salt solutions, thus bringing into solution notable amounts of the bases of these minerals. In fact a number of the primary minerals that are commonly present in soils in varying stages of decomposition and alteration react to some extent with the reagents which are ordinarily used in the determination of the replaceable bases. It is well known that calcium carbonate is soluble in solutions of ammonium salts. When calcareous soils are being investigated, it is not exceptional to find that the calcium equivalent of the dissolved carbonate may equal or even exceed the replaceable calcium.

The importance of these incidental reactions, with the possible exception of those involving calcium carbonate, is apparently not always appreciated by students of base exchange, for it is common to report the data obtained by analysis of an extract of the soil as if all the calcium, magnesium, potassium, and sodium found had been replaced. Moreover, the treatment of ohe subject at the hands of various investigators often gives the impression that the determination of the replaceable bases is a clear-cut and precise process similar to the determination of total nitrogen or total calcium. As a matter of fact this is far from being true. When we consider that the nature of the equi-

[1] Paper No. 217, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

librium between salt solutions and the exchange material makes it necessary to leach the soil for some time and with a considerable volume of the solution, that the salt solution inevitably dissolves or decomposes more or less of various minerals, that soils vary greatly in their leachability with the consequent variation in the length of time of contact between the salt solution and the soil, and that the true end point of the exchange reaction is often difficult to determine, it is evident that the determination of the replaceable bases is not a highly exact process. As a matter of fact sometimes special care is required to obtain good duplicate results with different samples of the same soil.

Ion exchange obviously denotes a reciprocal process. Upon treatment with a salt solution the soil not only gives up ions to the solution; it also absorbs an amount of base from the solution which is chemically equivalent to all of the ions that the base of the salt actually replaces from the soil. Substances which dissolve in the salt solution, or which react with the salt to form compounds that are unstable in the solution, will obviously yield quantities of base in excess of the amount that is absorbed. The extent to which solution and decomposition processes contribute to the results can be determined, however, by subtracting the sum of all cations that pass into the solution from the amount of that ion that is absorbed from the solution.

Failure to recognize that certain soils contain substances which undergo an exchange of their bases with barium, for example, but not with the alkalies, and that barium or calcium may be absorbed by soils from an alkaline solution, which elements may then be brought back into solution by the use of a neutral salt solution, but not necessarily as a result of ion exchange, has given rise to different methods for the determination of the replaceable bases, of replaceable H-ions, and of the base-exchange capacity of soils.

DETERMINATION OF REPLACEABLE BASES

Two types of method for the determination of the replaceable bases are in use at the present time. The method more commonly used involves the digestion and leaching of a weighed sample of the soil with a neutral salt solution or weak acid, the bases thus brought into solution being then determined. With the other method the replaceable bases are separated from the soil by electrodialysis and are determined tn the dialysate.

Mattson (10), Bradfield (1), Wilson (17), and others have compared the amounts of bases found by means of neutral salt extraction and by electrodialysis, and have reported fairly good agreement with soils from the humid and have reported fairly good agreement with soils from the humid region. The results obtained in this laboratory are consistent with this conclusion. Since the presence of soluble salts, alkaline earth carbonates, and easily decomposable silicates affect the results obtained by electrolialysis as well as by neutral salt or weak acid extraction, not attention has been given in this study to the electrodialysis method.

Gedroiz (3) pointed out that with soils containing carbonate a determination

of the carbonate (CO_3) content of the soil both before and after neutral salt extraction affords a basis for calculating the extent to which calcium carbonate affects the results. Kelley and Brown (7) have found that this method is accurate if the soil does not also contain magnesium carbonate. Although Hissink (4) and MacIntire (9) have concluded that magnesium carbonate is nonexistent in humid soils, this is not the case with certain soils of semiarid regions. In fact it is possible that certain alkali soils contain both normal and basic carbonate of magnesium in addition to calcium carbonate. Inasmuch as all of these carbonates are soluble to some extent in ordinary salt solutions, the universal applicability of the Gedroiz correction is doubtful.

Hissink's method (4) for the determination of replaceable calcium in soils which contain calcium carbonate is as follows:

> A 25-gm. sample of the soil is first digested for several hours at a temperature of about 70°C. with 250 cc. of *N* NaCl solution. The sample is then thrown on a filter and leached with fresh portions of the sodium chloride solution until two liters of leachate are obtained. The first liter of the leachate is kept separate from the second liter and calcium is determined in each liter separately. The calcium content of the first liter less that of the second liter is considered to be a measure of the replaceable calcium. This method involves the assumption that an equal amount of calcium carbonate is dissolved by each liter of the solution and that all of the replaceable calcium is removed by the first liter.

Burgess and Breazeale (2) proposed the use of 0.1 *N* $BaCl_2$ solution for the determination of the replaceable bases of calcareous soils. If a large quantity of soil and a minimum of the barium chloride solution are used, they concluded that the replaceable calcium and magnesium can be determined accurately by this method. Burgess and Breazeale concluded, on the basis of special solubility studies, that unimportant amounts of calcium carbonate are dissolved by barium chloride under the conditions of their method. Tjurin (15) holds, however, that "considerable and inconstant" amounts of calcium are brought into solution by the interaction of barium chloride and calcium carbonate.

Recently Magistad and Burgess (10) suggested the use of an ethyl alcohol solution of barium chloride instead of an aqueous solution of this salt. The solubility of calcium carbonate in ethyl alcohol is lower than in water; hence the error in replaceable calcium caused by the solubility of calcium carbonate is decreased. They suggest that for accurate results a correction should be applied to the calcium found in the leachate on the basis of the theoretical solubility of calcium carbonate in this reagent.

According to Tjurin's method (15), 10 gm. of soil is leached with successive 500-cc. portions of *N* NaCl. The total content of carbonate and bicarbonate is determined in each portion of the leachate by titration with 0.02 *N* HCl methyl orange being used as indicator. Calcium and magnesium are also determined in each portion. When the sum of the calcium and magnesium no longer exceeds the carbonate and bicarbonate content of the leachate, the replacement of the calcium and magnesium is considered to be complete. The

difference between the sum of the calcium and magnesium in the several portions of the leachate and the total carbonate and bicarbonate expressed as chemical equivalents, represents the sum of the replaceable calcium and magnesium.

Novak and Malac (12) and Hissink (6) have recently made comparative studies on the Hissink method and the ammonium chloride methods as outlined by Gedroiz (3) and by Kelley and Brown (7). The results were widely divergent. It seems probable that in these investigations no correction was made for the solution of calcium carbonate by ammonium chloride. If this be the case, then the conclusions concerning the relative accuracy of these methods are invalid.

In view of the limited and somewhat uncertain nature of previous studies on the various methods for the determination of replaceable calcium in calcareous

TABLE 1

Replaceable Ca as determined by different methods

METHOD	MILLIEQUIVALENTS PER 100 GM. SOIL	
	Ca	NH_4 absorbed
NH_4Cl	0.00*	21.24
	0.00	21.24
Hissink	17.23	.....
	17.01	.....
Burgess and Breazeale	25.83	.....
	26.08	.....

* Calcium equivalent of carbonate dissolved exceeded the total calcium in leachate.

soils, it was decided to compare the ammonium chloride method, the Hissink method, and the Burgess and Breazeale method[2] on the carbonate-containing soil from California. The soil used is a dark-colored silt loam low in water-soluble constituents, and contains 6.9 per cent insoluble carbonate (CO_3). The methods as outlined by the original authors were followed as closely as possible. With the ammonium chloride method, total carbonate (CO_3) was determined both before and after the extraction and a correction was applied to the calcium data on the assumption that magnesium carbonate was non-existent in this soil. The data reported in table 1 reveal that this assumption was incorrect, for the equivalent of the dissolved carbonate exceeded the total calcium found; hence a part of the carbonate in this soil must be normal or basic magnesium carbonate.

The replaceable calcium found by the barium chloride method of Burgess

[2] When this part of the investigation was made the method proposed by Magistad and Burgess had not been published.

and Breazeale was somewhat in excess of the NH_4 absorbed from ammonium chloride. Whether this difference was occasioned by incomplete replacement of calcium and magnesium by NH_4, or by errors that are inherent in the barium chloride method can not be stated definitely. Neither can the accuracy of the data obtained by the Hissink method be stated at present.

Special studies on the Hissink method were made to determine more definitely the approximate magnitude of the errors involved. For this purpose a neutral soil free from carbonate and low in water-soluble salts was used. Ten-gram samples of this soil, to which a known amount of calcium carbonate was added, were digested with 100 cc. of *N* NaCl at 70°C. over night. These solutions were then filtered and the soil was transferred quantitatively to a filter and leached with normal sodium chloride until 400 cc. of leachate was obtained. This amount of leaching is equivalent to 1,000 cc. for 25 gm. of soil. The leaching was then continued until another 400 cc. was obtained. Calcium

TABLE 2

Effect of $CaCO_3$ on the determination of replaceable Ca by the Hissink method (digested at 70°C.)

SAMPLE	MILLIEQUIVALENTS Ca PER 100 GM. SOIL		
	First 400 cc.	Second 400 cc.	Difference
Soil alone	8.54	0.00	8.54
	8.40	0.00	8.50
Soil + 2½ per cent $CaCO_3$	16.30	3.32	12.98
	16.60	3.12	13.48
	16.00	3.32	12.68
	16.70	3.32	13.38

was determined in both portions. Similar experiments were made with this soil without adding calcium carbonate. The results are recorded in table 2. They show that under the conditions of this experiment a greater amount of calcium carbonate was dissolved in the first than in the second portion of the leachate, as is indicated by the fact that the difference between the calcium content of the first and second portions is considerably greater than that found where no calcium carbonate was added.

Since the samples used in the foregoing experiment were first digested at an elevated temperature and then filtered and leached at ordinary laboratory temperature, as was recommended by Hissink, it seemed desirable to determine whether this preliminary digestion influenced the results. Accordingly another experiment was made with the same soil in which the preliminary digestion was made at room temperature. In all other respects the same technique was employed as in the previous experiment. The results are recorded in table 3. It will be noted that the temperature factor materially affected the solubility of calcium carbonate, but had no appreciable effect on the replacement of calcium.

By calculation it was found that the solubility of calcium carbonate was 0.098 gm. a liter in the first experiment (heated to 70°C.) and 0.062 gm. a liter in the second experiment (room temperature). Each of these quantities exceeds the theoretical solubility of calcium carbonate in normal sodium chloride solution. Without going into a theoretical discussion of this fact it seemed possible that different results might be obtained with soils which contain calcium carbonate naturally.

Accordingly samples of three different calcareous soils consisting of 25 gm. each were digested at 70°C. over night with 250 cc. of neutral *N* NaCl. The soil and solution were then quantitatively transferred to a filter and leached

TABLE 3

Effect of $CaCO_3$ on the determination of replaceable Ca by the Hissink method (room temperature)

SAMPLE	MILLIEQUIVALENTS Ca PER 100 GM. SOIL		
	First 400 cc.	Second 400 cc.	Difference
Soil alone	8.40	0.00	8.40
Soil + 2½ per cent $CaCO_3$	13.45	3.81	9.64

TABLE 4

The solution of $CaCO_3$ by normal NaCl under the conditions of the Hissink method

SOIL NUMBER	MILLIEQUIVALENTS PER 100 GM. SOIL		
	First liter	Second liter	
	CO_3	CO_3	Ca
709	1.84	1.32	1.28
709	1.96	1.32	1.28
534	2.72	2.76	3.44
534	2.64	2.76	3.28
8563	3.20	2.40	3.56
8563	3.24	2.28	3.16

until two liters of leachate had been obtained. The amounts of carbonate dissolved in the first and second liters, respectively, were determined by titrating 500 cc. with 0.1 *N* H_2SO_4, methyl orange being used as indicator. The calcium content of the second liter was also determined. The results, corrected for water-soluble carbonate, are shown in table 4.

It will be noted that the amount of carbonate found in the first liter of leachate from two of the soils is slightly in excess of that found in the second liter. If an elevated temperature had not been used in the preliminary digestion, it is probable that less carbonate would have appeared in the first liter of the leachate. With soils 534 and 8563 the second liter contained slightly more calcium than carbonate. It is probable, as was pointed out by Turner (16)

and Tjurin (15), that not all of the exchangeable calcium will be replaced by leaching 25 gm. of a highly calcareous soil with 1 l. of *N* NaCl solution.

The preceding data indicate that, should a greater amount of calcium carbonate be dissolved by the first liter of sodium chloride solution than by the second, the error thus introduced into the calcium data might be compensated for to some extent by the fact that not quite all of the exchangeable calcium is replaced by the first liter. Hence, upon subtracting the quantity of calcium found in the second liter from that in the first, approximately accurate figures for replaceable calcium may be obtained.

The next experiment was made with the alcoholic barium chloride method as proposed by Magistad and Burgess. Ten-gram samples of the same carbonate-free soil that was used in the experiments reported in table 2 were digested at room temperature with 200 cc. of the barium chloride reagent both with and without the addition of calcium carbonate. After occasional shaking for two hours the soil was transferred to a filter and leached until 800 cc. of leachate had

TABLE 5

Replaceable Ca as determined by the alcoholic-$BaCl_2$ method of Magistad and Burgess

SAMPLE	MILLIEQUIVALENTS Ca PER 100 GM. SOIL		
	First 400 cc.	Second 400 cc.	Difference
Soil alone	8.34	0.00	8.34
	8.44	0.00	8.44
Soil + 2½ per cent $CaCO_3$	9.88	1.25	8.63
	9.84	1.30	8.54
	9.78	1.35	8.43

been obtained. Both the first and second 400-cc. portions of the filtrate were analyzed for calcium by the method as outlined by Magistrad and Burgess. The results are given in table 5. By subtracting the quantity of calcium found in the second 400 cc. of leachate from that of the first, approximately correct figures for replaceable calcium were obtained. These data indicate that by making a correction for the dissolved carbonate this method gives reasonably accurate results. Comparison of the data reported in tables 3 and 5 reveals that the solubility of calcium carbonate is considerably greater in an aqueous solution of sodium chloride than in alcoholic barium chloride.

Inasmuch as the method of Magistad and Burgess entails considerable analytical detail in the separation of calcium from barium, the use of an alcoholic solution of potassium chloride was suggested. Accordingly, 10-gm. samples of the soil used in the previous experiment, both with and without the addition of calcium carbonate, were digested at room temperature for one hour with 200 cc. of 0.2 *N* KCl dissolved in 63 per cent ethyl alcohol. The suspensions were then filtered and the soil was leached until 800 cc. of leachate

had been obtained. Calcium was determined in the first and second 400-cc. portions of the leachate. The results are given in table 6.

Comparison of the data reported in tables 5 and 6 shows that the solubility of calcium carbonate is slightly lower in alcoholic potassium chloride than in alcoholic barium chloride. Subtracting the quantity of calcium found in the second 400 cc. from that in the first, gives good agreemnnt between the values.

The foregoing experiments suggest that approximately accurate determinations of replaceable calcium can be made in calcareous soil by several different methods, provided, however, that other easily decomposable or soluble calcium compounds are not present. With soils which contain easily soluble silicates of calcium or gypsum, no method is known to the writers by which it is possible to determine the replaceable calcium. Since calcium carbonate is only slightly soluble in alcoholic potassium chloride, it is possible that the silicates of calcium are also quite insoluble in this solution. If this be the case,

TABLE 6

Replaceable Ca as determined with alcoholic KCl

SAMPLE	MILLIEQUIVALENTS Ca PER 100 GM. SOIL		
	First 400 cc.	Second 400 cc.	Difference
Soil alone	8.30	0.00	8.30
	8.20	0.10	8.10
Soil + 2½ per cent $CaCO_3$	9.40	1.07	8.33
	9.50	0.99	8.51

then this method would be applicable to all soils except those which contain gypsum.

By determining the replaceable potassium and sodium by the use of an ammonium salt, the replaceable calcium with alcoholic potassium chloride or barium chloride, and the total content of replaceable bases by the NH_4 absorption method (discussed more fully in the second part of this paper) it is possible to determine the replaceable magnesium by difference.

DETERMINATION OF BASE-EXCHANGE CAPACITY BY THE NH_4-ABSORPTION METHOD

"Base-exchange capacity," as we use the term, refers to the total quantity of cations which the soil is capable of holding in a form that is replaceable by, and stable in, neutral solutions of calcium, magnesium, potassium, sodium, and ammonium salts.

The Hissink (5) method for the determination of the base-exchange capacity first determines the replaceable bases and then determines the content of replaceable H ions by a special method. The sum of the quantities found, ex-

pressed as milliequivalents, represents the base-exchange capacity (*T*). Hissink's method (5) for determining the H ion involves the treatment of the soil with an excess of barium hydroxide. Hissink (6) holds that the replaceable bases are present in the soil as salts of weak acids and that the salts hydrolyze to some extent when brought into contact with water. Consequently these salts can be completely saturated with a strong base, such as calcium, only in regions of high alkalinity (pH 10 or more). This view may be theoretically sound. It seems to be of doubtful value in connection with soil investigations, however, for the base-exchange material probably neither was formed under conditions of high alkalinity, nor do such conditions exist in ordinary soils. Acid soils become alkaline when an amount of barium equivalent to Hissink's *T*-*S* values is added, but the same is true of colloidal silica and many other substances.

When we consider that, in addition to the base-exchange material, other soil substances, such as silica, the oxides of iron and aluminum, and various primary and secondary minerals, are able to absorb barium hydroxide, and the barium hydroxide thus absorbed is readily brought back into solution upon leaching with a neutral salt solution, it is evident that the determination of the barium that has been absorbed from barium hydroxide does not give reliable evidence as to the replaceability of the absorbed barium.

Several years ago Kelley and Brown (7) proposed the NH_4- absorption method for the determination of the base-exchange capacity. According to this method the soil is first saturated with NH_4 and then the absorbed NH_4 is determined. Formerly ammonium chloride was used to saturate the soil with NH_4. Since it is not possible to effect complete replacement of H ions[3] by ordinary leaching with ammonium chloride, Kelley and Brown (8) later recommended the preliminary treatment of acid soils with an excess of barium hydroxide. Their method is based on the principle that all of the replaceable bases of a soil, whether it be completely saturated with base or only partially so, can be replaced by NH_4.

A number of other methods for the determination of base-exchange capacity, either directly or indirectly, have been proposed, but inasmuch as the principles involved do not differ materially from those of the Hissink and the Kelley and Brown methods, they will not be discussed here.

The principles underlying the NH_4-absorption method appear to be reasonably sound. The total NH_4-absorbing capacity of a soil is a quantity which probably has as much agricultural significance as Hissink's (*T*) value, and, perhaps most important of all, this quantity gives a measure of total exchangeable ions, as ordinarily understood. Hence its determination makes it possible to distinguish between solution and decomposition processes, on the one hand, and replacement reactions, on the other.

[3] The term "replaceable H ion," as used here and henceforth in this paper, refers to the quantity that is equivalent to the amount of barium hydroxide necessary to bring a soil to pH 7.0.

The advantages of ammonium salts over the other neutral salts that have been recommended are: NH_4 does not occur to any important extent in the natural soil; the absorbed and therefore replaceable NH_4 can be determined readily and accurately; NH_4 probably does not form insoluble compounds with components of the soil other than the exchange complex. Such substances, for example, as the addition compounds that are formed by an excess of calcium hydroxide or barium hydroxide, the precipitation products that may occur naturally or are readily formed artificially in alkali soils, and the intermediate and unstable products of weathering that occur in the relatively immature soils of semiarid regions, do not form insoluble compounds with NH_4.

The results of special investigations with reference to the completeness of replacement of cations by NH_4 and the precise determination of the absorbed NH_4 are presented in the following pages.

Effect of time of digestion

Kelley and Brown (7) found that preliminary digestion of the soil with ammonium chloride at 70°C., followed by leaching with ammonium chloride

TABLE 7

Effect of time of digestion on the amount of NH_4 absorbed from ammonium acetate

TIME OF DIGESTION	MILLIEQUIVALENTS NH_4 ABSORBED PER 100 GM. SOIL
20 minutes	26.25
15 hours	28.96
60 hours	29.72
72 hours	29.44

solution, brought about the absorption of a greater amount of NH_4 than mere leaching at room temperature. To determine the effect of more prolonged heating, 10-gm. samples of a neutral, carbonate-free soil, were digested with 250 cc. of neutral *N* CH_3COONH_4 (ammonium acetate) at 70°C. for periods of 20 minutes, 15, 60, and 72 hours. The soils were then filtered and leached until a volume of 400 cc. had been obtained. After removing the electrolyte by washing with methyl alcohol the absorbed NH_4 was determined by aeration.[4] The results are reported in table 7. These data show that complete replacement was not effected when the digestion was limited to 20 minutes but became approximately complete within 15 hours.

Replacement of H ions

Inasmuch as complete replacement of H ions is not effected by ordinary leaching with ammonium chloride, Kelley and Brown (8) recommended the preliminary treatment of the soil with an excess of barium hydroxide as a

[4] A modification of the well-known aeration method for the determination of NH_4 in soils has been worked out by A. P. Vanselow of this laboratory. This method has been used in all of the work reported in this paper.

means of replacing the H ions with barium, thus bringing the soil into a state of complete base saturation. Recently Schollenberger (14) suggested the use of ammonium acetate in place of ammonium chloride. Among other advantages, this salt will effect more complete removal of replaceable H ions than will ammonium chloride. That acetates will replace more H ions under ordinary leaching conditions than the corresponding chlorides is well known. Parker (13) has recently shown that the amounts of replaceable H ions, as determined by titrating acid soils to pH 7.0 with barium hydroxide and by the barium acetate method, are practically identical. His data suggest that complete replacement of H ions might be effected by leaching with neutral ammonium acetate solution.

In order to study this point, a comparison was made on a series of soils of the amounts of NH_4 absorbed from ammonium acetate both with and without preliminary treatment of the sample with barium hydroxide. With the barium

TABLE 8

NH_4 absorbed from ammonium acetate with and without preliminary $Ba(OH)_2$ treatment

SOIL	pH	MILLIEQUIVALENTS NH_4 ABSORBED PER 100 GM. SOIL	
		Without preliminary treatment	Treated with $Ba(OH)_2$
431*	3.65	29.66	30.48
7576	4.77	61.45	62.11
3232	5.19	7.98	8.43
7526	5.30	46.71	46.74
11952	5.15	15.26	16.51
7092	7.41	15.93	15.77
7891	7.72	3.33	3.45
7575	5.80	108.90	115.15

* This sample had first been leached with 0.05 N HCl.

hydroxide treated series, 10-gm. samples were digested with 100 cc. of 0.1 *N* $Ba(OH)_2$ for 24 hours. The soils were then filtered and taken up with 100 cc. of neutral *N* CH_3COONH_4. These suspensions were digested at 70°C. for 15 hours, filtered, and leached until the leachate was free from calcium and barium. The excess of ammonium acetate was washed out with methyl alcohol and the absorbed NH_4 was determined by aeration. The same general technique was used with the other series. The results are given in table 8. With the exception of a peaty soil, 7575, the results of the two series are in reasonably close agreement. They are in harmony with Parker's (13) data. Whether the slight increases in absorbed NH_4 incident to barium hydroxide treatment of the samples, were occasioned by the replacement of small quantities of H ions that were not replaced directly by NH_4, or to the synthesis, under the influence of barium hydroxide, of a compound possessing base-exchange properties, or to some other factor, is not known. In any case it appears that

for all practical purposes neutral ammonium acetate will replace the H ions completely without preliminary treatment of the soil with barium hydroxide.

Effect of calcium carbonate on the absorption of NH_4

In view of the high solubility of calcium carbonate in ammonium acetate, it is possible that the calcium-ion concentration produced by the solution of calcium carbonate might be sufficient to prevent the complete replacement of exchangeable calcium by NH_4. To test this point, different quantities of calcium acetate were added to a series of normal ammonium acetate solutions and these solutions were then employed in the determination using a carbonate-free soil. The results reported in table 9 show that a concentration of 10 p.p.m. calcium exerts no measurable influence on the absorption of NH_4 from a normal

TABLE 9

Influence of Ca ions on absorption of NH_4 by soils

Ca in solution	Milliequivalents NH_4 absorbed per 100 gm. soil
p.p.m.	
0	28.96
5	28.70
10	29.22
500	26.44
1,000	25.90

TABLE 10

Influence of $CaCO_3$ on the absorption of NH_4

Per cent $CaCO_3$ added to soil	Milliequivalents NH_4 absorbed per 100 gm. soil
0.00	28.96
0.09	29.08
2.91	29.28
4.75	26.83
6.55	25.82

solution of ammonium acetate, but that concentrations of 500 and 1,000 p.p.m. do exert some effect.

In another experiment varying quantities of purified c.p. calcium carbonate were added to 10-gm. samples of a neutral carbonate-free soil. The samples were then treated with normal ammonium acetate in the usual way. The absorbed NH_4 is reported in table 10. These data demonstrate that calcium carbonate, if present in relatively large amount, may interfere with the replacement of calcium and therefore affect the accuracy of the results. In order to guard against this possibility the sample should be leached with ammonium acetate until the leachate is practically free from calcium.

Before making a direct determination of the absorbed NH_4 it is, of course, necessary to remove the occluded ammonium salts. For some time we have

leached out the ammonium salts with methyl alcohol, using the Nessler test to determine the end point. In connection with studies on this point it was found that the methyl alcohol leachate continued to give an appreciable test for NH_4 indefinitely. In an effort to determine whether this continued test for NH_4 represented traces of electrolyte still remaining in the soil or the loss of NH_4 split off from the exchange complex, the following study was made:

Six 10-gm. samples of a neutral soil were digested and leached with normal neutral ammonium chloride in the usual way. They were then washed with 200 cc. of double-distilled methyl alcohol. At this point the leachate gave only a faint test for NH_4. Three of the samples were then washed with an additional 500 cc. of methyl alcohol. NH_4 was then determined in all the soil samples by the aeration method. NH_4 and chlorine determinations were also made in the last 500 cc. of washings.

The results are given in table 11. These data indicate fairly conclusively that NH_4 may be lost from the exchange complex by washing with an excess of methyl alcohol. Inasmuch as the alcohol leachings were perfectly clear,

TABLE 11

Loss of NH_4 from soil by prolonged washing with methyl alcohol

VOLUME OF METHYL ALCOHOL USED	MILLIEQUIVALENTS PER 100 GM. SOIL		
	NH_4 absorbed	NH_4 in last 500 cc. of washings	Chlorine in last 500 cc. of washings
cc.			
200	28.17	....	....
200	28.32	....	....
200	28.57	....	....
700	27.17	0.68	Trace
700	27.17	0.80	Trace
700	27.27	....	Trace

the loss of NH_4 was probably not due to the passage of colloidal material through the filter paper.

The methyl alcohol used in the foregoing experiment was found to be distinctly acid. Thus far we have been unable to obtain neutral methyl alcohol even by distillation over lime and sodium hydroxide. Apparently the available supply of this alcohol contains some aldehyde or ketone, which oxidizes to an acid in the vapor phase during distillation. When allowed to stand in contact with sodium hydroxide for several weeks, the alcohol became brown and viscous, indicative of the presence of aldehydes or ketones.

Further studies upon the losses of NH_4 occasioned by leaching with methyl alcohol strongly indicated that the losses noted in the last experiment were due to traces of acid in the alcohol.

To test this point further one quantity of redistilled methyl alcohol was adjusted to pH 7.0 with dilute ammonium hydroxide and another with sodium hydroxide. These solutions were then used in comparison with the original

methyl alcohol. The soil samples were first saturated with NH_4 by leaching with ammonium acetate solution and the occluded ammonium acetate was then displaced by leaching with neutral ammonium chloride. The electrolyte was removed by leaching with the aforementioned supplies of methyl alcohol, the chlorine test being used to determine the end point. The results are shown in table 12.

These data indicate that the loss of NH_4, occasioned by the acidity of the methyl alcohol, can be overcome by neutralizing the alcohol with ammonium hydroxide. The data also indicate that it is not permissible to neutralize the

TABLE 12

Influence of pH of methyl alcohol upon the determination of the absorbed NH_4

pH OF ALCOHOL	VOLUME OF LEACHINGS	MILLIEQUIVALENTS NH_4 ABSORBED PER 100 GM. SOIL
	cc.	
5.2	300	28.9
7.0 (neutralized with NH_4OH)	220	31.3
7.0 (neutralized with NH_4OH)	300	31.9
7.0 (neutralized with NH_4OH)	500	31.5
7.0 (neutralized with NaOH)	400	28.0

TABLE 13

NH_4 absorbed by soil as determined by making correction for the electrolyte left in the soil

Milliequivalents per 100 gm. soil

TOTAL NH_4	NH_4 AS NH_4Cl	DIFFERENCE = NH_4 ABSORBED
44.73	13.42	31.31
45.62	14.50	31.12
50.40	19.20	31.20

alcohol with sodium hydroxide, for the sodium ions thus introduced into the solution may replace a part of the absorbed NH_4.

In order to eliminate the necessity for leaching with methyl alcohol, an experiment was made to determine the amount of electrolyte that is left in the soil after it has been saturated with NH_4. Where ammonium chloride is used, determinations of NH_4 and chlorine in the sample make it possible to estimate the amount of NH_4 that is held in exchangeable form without the necessity of leaching out the electrolyte.

The samples, after treatment with the ammonium salt, were transferred directly to Kjeldahl flasks and NH_4 was determined by aeration. The amount found obviously included both the absorbed NH_4 and that present as ammo-

nium chloride. After the aeration was complete the contents of the flasks were acidified with nitric acid and chlorine determinations were made. By subtracting the NH_4 equivalent of the chlorine from the total NH_4 found, the absorbed NH_4 is obtained. The data are reported in table 13. The close agreement between the results obtained by this method and those obtained by washing out the electrolyte with methyl alcohol adjusted to pH 7.0 with ammonium hydroxide, indicates that either method may be used with confidence.

As has already been stated, the absorbed NH_4 was determined by the aeration method. Special experiments made to test the accuracy of this method have shown that it permits of practically complete recovery of the absorbed NH_4. Under the conditions of this method the organic nitrogen compounds are not odidized to NH_4, whereas more or less oxidation may take place when distillation methods are used.

CONCLUSIONS

The determination of the replaceable bases of soils is not highly exact. The results are likely to be complicated by solubility and decomposition processes, which take place between the solutions used and various constituents of the soil. Such constituents are probably most important in relatively immature soils of dry climates.

The Hissink sodium chloride method, the alcoholic barium chloride method of Magistad and Burgess, and the method involving the use of alcoholic potassium chloride all give reasonably accurate results for the determination of replaceable calcium in calcareous soils, provided other soluble or decomposable calcium compounds are absent from the sample. If the soil contains such compounds it is probable that the replaceable calcium cannot be determined accurately by any method.

The base-exchange capacity of the soil can be determined by digesting and leaching the sample with normal ammonium acetate solution. This solution brings about approximately complete replacement of the H ions without the necessity of treating the sample with an excess of alkali. It was found that methyl alcohol is useful for the removal of the occluded electrolyte but that it is necessary to employ as nearly neutral methyl alcohol as possible. If the methyl alcohol is acid, its H ions may replace more or less of the absorbed NH_4 and thus introduce an appreciable error. The absorbed NH_4 can be accurately determined by aeration in the presence of sodium carbonate.

REFERENCES

(1) BRADFIELD, R. 1927 The use of electrodialysis in physico-chemical investigations of soils. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 264–278.

(2) BURGESS, P. S., AND BREAZEALE, J. F. 1926 Methods for determining the replaceable bases of soils, either in the presence or absence of alkali salts. Ariz. Agr. Exp. Sta. Tech. Bul. 9.

(3) GEDROIZ, K. K. 1918 Contribution to the method of determining the zeolitic bases in the soil. *Zhur. Opyth. Agron.* (Russian) 19: 226–244.

(4) HISSINK, D. J. 1922 Beitrag zur Kenntnis der Adsorptionsvorgänge im Boden. Methode zur Bestimmung der austauschfähigen oder absorptiv gebundenen Basen im Boden und die Bedeutung dieser Basen für die Prozesse, die sich im Boden abspielen. *Internatl. Mitt. Bodenk.* 12: 81–172.

(5) HISSINK, D. J. 1925 Base exchange in soils. *Trans. Faraday Soc.* 20: 551–566.

(6) HISSINK, D. J. 1927 Soil adsorption. *Proc. and Papers First Internatl. Cong. Soil Sci.* 1: 170–189.

(7) KELLEY, W. P., AND BROWN, S. MELVIN 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.

(8) KELLEY, W. P., AND BROWN, S. M. 1927 Base unsaturation in soils. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 1–17.

(9) MCINTIRE, W. H., WILLIS, L. G., AND HARDY, J. I. 1914 The non-existence of magnesium carbonate in humid soils. Tenn. Agr. Exp. Sta. Tech. Bul. 107.

(10) MAGISTAD, O. C., AND BURGESS, P. S. 1928 The use of alcoholic salt solutions for the determination of replaceable bases in calcareous soils. Ariz. Agr. Exp. Sta. Tech. Bul. 20.

(11) MATTSON, SANTE 1926 Electrodialysis of the colloidal soil material and the exchangeable bases. *Jour. Agr. Res.* 33: 553–567.

(12) NOVAK, VACLOV, AND MALAC, BOH. 1927 Eine Studie über die ausstauschbaren Basen im Boden. *Vestnik, Bul. Czechoslovak Acad. Agr., Rocnik* III., *Cislo* 5: 1–7.

(13) PARKER, F. W. 1929 The determination of exchangeable hydrogen in soils. *Jour. Amer. Soc. Agron.* 21: 1030–1039.

(14) SCHOLLENBERGER, C. J. 1927 Exchangeable hydrogen and soil reaction. *Science* (n.s.) 65: 552–553.

(15) TJURIN, I. W. 1927 Method of determination of exchangeable calcium and magnesium in soils containing alkaline earth carbonates. *La Pedologie* 22: 5–24.

(16) TURNER, P. E. 1928 An investigation of the method of Page and Williams for the determination of the saturation capacity of soils. *Jour. Agr. Sci.* 18: 257–265.

(17) WILSON, B. D. 1928 Exchangeable cations in soils as determined by means of normal ammonium chloride and electrodialysis. *Soil Sci.* 26: 407–422.

CROSS INOCULATION WITH RHIZOBIUM RADICICOLUM

VICTOR BURKE AND NELSON J. HOHL

State College of Washington

Received for publication March 10, 1930

Attempts to modify the pathogenicity or symbiotic activity of *Rhizobium radicicolum* have generally met with failure. It has never been satisfactorily demonstrated that the root-nodule bacteria can be modified to grow on the rootlets of non-legumes. Cross inoculation between legume groups has been recorded but the possibility of extending the power of cross inoculation, if present, or of causing it to develop, if absent, beyond the natural limits of the strain of *Rhizobium radicicolum* has not been satisfactorily demonstrated (3). It is obvious that if cross inoculation between legumes cannot be induced or increased, it is useless to attempt inoculation of non-legumes with legume organisms.

In increasing the virulence of animal pathogens various procedures are followed. Growing the organism on the blood of the host, injecting the organism into tissues where it is less subject to the natural immunity of the host, or injecting massive doses to reduce the resistance of the host or exhaust its defensive mechanism, frequently results in the development of increased virulence. By these methods it is possible to cause non-pathogenic organisms to acquire some degree of pathogenicity, and pathogenic organisms which have lost their virulence to regain it. The degree of increase in pathogenicity is limited to a greater or less extent according to the species. Both the factors of adaptation and selection take part in the changes that occur. That *Rhizobium radicicolum* can be modified by exposure and selection has been demonstrated by Burke and Burkey (1).

Similar methods were applied by the authors in attempting cross inoculation between the different groups of legumes. It was also considered that if failure of cross inoculation depended on the inhibition of heterologous organisms by the plant juice this inhibitory factor might be utilized as a means of identifying strains.

EXPERIMENTAL

Nodule producing organisms were isolated from nodules on the rootlets of red clover (group 1), vetch (group 4), and alfalfa (group 2). To eliminate existing variations as an interfering factor, in making isolations from the nodules several typical colonies were selected and a composite stock culture was made from them. Each strain isolated produced nodules on the homologous but not on the heterologous legumes.

The legume seeds were inoculated and planted, and the plants were kept under observation for three months or longer in many cases. In some cases nodules were produced in 21 days. The method of growing the plants was that of Garman and Didlake (2). Uninoculated seeds were planted as controls. Each inoculation was in triplicate.

Experiment 1

The object of experiment 1 was to determine the effect of exposure to heterologous legume extract on the specificity of strains of *Rhizobium radicicolum*.

An alfalfa extract was prepared by grinding alfalfa roots in distilled water and sterilizing by filtering through a Berkefeld "W" filter. The filtrate was clear, yellowish, and transparent.

The vetch and red clover strains of *Rhizobium radicicolum* were grown on this medium for three months. Transplants were made every two weeks. The medium was favorable, as the organisms produced heavy growths. This favors the view that failure to produce nodules on heterologous legumes is not due to any inhibitory action of the plant juice. In order to avoid introducing any unnecessary changes, the plant juice used in this experiment was not sterilized by heat.

The vetch and red clover strains were next placed on alfalfa seeds and these planted and examined as previously described. As controls, vetch and red clover seeds were inoculated and planted as well as uninoculated seeds. The inoculated alfalfa seedlings failed to develop nodules. The vetch and red clover seedlings developed nodules. All other seedlings failed to develop nodules.

The results obtained favor the view that the nodule-forming character of *Rhizobium radicicolum* is highly group specific and not readily modified by exposure to the plant juice of a legume from another group. The experiment was repeated with various modifications in the technique used. The alfalfa root extract was added to equal parts of Ashby's medium and the organism grown on this. Extracts were made from the leaves and stems. Extracts from leaves, stems, and roots were sterilized by heat instead of by filtrations. In no case did prolonged growth on these extracts alter the nodule-production character of the vetch and red clover strains.

Since prolonged exposure to alfalfa extract failed to alter the specificity of red clover and vetch strains, these strains were exposed to living tissue. It was hoped that this experiment would determine whether the nodule-forming requirements of the strains can be modified by this method and whether failure to form nodules on heterologous legumes is due to the inhibitory action of the plant tissue.

Experiment 2

The object of experiment 2 was to determine the effect of exposure to living plant tissue on the specificity of strains of *Rhizobium radicicolum*.

Well-developed alfalfa plants with a stalk about one-half inch in diameter and without nodules were removed from the soil and washed thoroughly. The roots were sterilized in a 1:1,000 mercuric chloride solution for 15 minutes. They were then washed in several changes of sterile water and placed in flasks containing a nutrient solution. A cotton wrapping about the stalk at the mouth of the flask prevented contamination.

The nutrient solution remained sterile, indicating a satisfactory technique. The plants were now removed from the flasks and a "Λ" shaped cut was made through the outer layer of the root. The flap was loosened, a loopful of culture inserted, and the flap pressed into position. Two alfalfa plants were thus inoculated with the vetch strain and two with the red clover strain of nodule-forming organisms. The alfalfa plants were returned to the flasks and kept for three months. The "Λ"-shaped incision was above the nutrient solution, which remained sterile. The plants were then removed, the "Λ"-shaped flaps again loosened, and cultures made. In each case the strain inoculated was isolated in pure culture. Each strain was tested for nodule production of the homolgous legume and on alfalfa. In each case the strain produced nodules on the homologous legume but not on alfalfa.

The results obtained indicate that specific nodule formation of strains of *Rhizobium radicicolum* is not readily modified by exposure to living plant tissue. This and the preceding experiment also indicate that failure to produce nodules is not due to any bactericidal action of the plant tissue. Bacteriostatic action may occur in the living tissue but since none occurred in fresh plant extract and the organism survived for a long time in living tissue, we must consider that such action, if present, is slight.

In our experiment, we attempted to modify only the nodule-producing organism. Since nodule formation depends on both the legume and the bacteria, positive results might be obtained by modifying both at the same time. The practical value of artificially modifying the legume plant is obscure. Natural modifications do occur in nature and the duplication of these experimentally to determine the possibility of cross inoculation is worthy of attention.

The possibility of separating the different strains of *Rhizobium radicicolum* by the rate of growth in legume extract was considered. Experiment 1 demonstrated that little, if any, bacteriostatic action for heterologous strains was present in legume extract. The following experiment was designed to determine this more accurately.

Experiment 3

The object of experiment 3 was to determine the comparative rate of growth of strains of *Rhizobium radicicolum* in homologous and heterologous legume extract.

Extracts of red clover, vetch, and alfalfa were prepared by macerating the roots in water and sterilizing by filtering through a Berkefeld "W" filter. A sample of each extract was inoculated with red clover, vetch, and alfalfa strains

of *Rhizobium radicicolum*. The cultures were examined after 12, 24, and 30 hours. No differences between the rate of growth in the homologous and heterologous extracts could be detected.

The red clover strain cultures showed definite growth in 12 hours, the alfalfa strain in 24 hours, and the vetch strain in 30 hours. Other cultures were obtained and tested for rate of growth to determine whether certain strains consistently grew more rapidly in legume extract. The results, given in table 1, are not definite. They indicate some variation in rate of growth between strains and between different cultures of the same strain. Whether this difference can be utilized to separate strains remains to be determined.

TABLE 1

Rate of growth of strains in legume extracts and in plain broth

STRAIN, BURRILL CLASSIFICATION	VETCH EXTRACT			RED CLOVER EXTRACT			ALFALFA EXTRACT			PLAIN BROTH		
	12 hours	24 hours	30 hours	12 hours	24 hours	30 hours	12 hours	24 hours	30 hours	12 hours	24 hours	30 hours
1*	x†	xx	...	x	xx	...	x	xx	...	x	xx	...
1 Wis.	x	xx	...	x	xx	...	x	xx	...	x	xx	...
1 W.S.C.	x	x	...	x	xx	...	x	xx	...	x	xx	...
2*	—	x	xx	—	x	xx	—	x	xx	—	x	xx
2*	x	xx	...	x	xx	...	x	xx	...	x	xx	...
2 Wis.	x	xx	...	x	xx	...	x	xx	...	x	xx	...
2 W.S.C.	—	—	x	—	—	x	—	—	x	—	—	x
4*	—	—	x	—	—	x	—	—	x	—	—	x
4 Wis.	—	x	x	—	x	x	—	x	x	—	—	x
4 W.S.C.	—	x	x	—	x	x	—	x	x	—	x	x
5 Wis.	—	—	x	—	—	x	—	—	x	—	—	—
5 W.S.C.	—	x	x	—	x	x	—	x	x	—	—	x
6 W.S.C.	—	x	x	—	x	x	—	x	x	—	x	x

* Isolated for these experiments. Wis. Obtained from the University of Wisconsin. W.S.C. Washington State College laboratory cultures.

† x indicates faint growth; xx, heavy growth.

CONCLUSIONS

Legume tissue and extract do not have bactericidal action on heterologous strains of *Rhizobium radicicolum*. The extract alone does not have bacteriostatic action and probably the tissue does not.

Exposure to heterologous legume tissue and extract does not cause strains of *Rhizobium radicicolum* to change their specificity. Cross inoculation between certain of the legume groups is not made possible by this method. Whether the symbiotic activity of a strain for homologous legumes can be increased by exposure to plant juice or living plant tissue was not determined. It is probable that the limit of symbiotic activity of any strain depends upon exposure resulting in increased adaptation to the host and selection of the most active cells.

Different strains and different cultures of the same strain vary in their rate of growth in legume extract. The rate of growth in homologous and heterologous legume extract is the same. Whether the rate of growth of different strains varies sufficiently to be useful in identification is unknown.

REFERENCES

(1) BURKE, VICTOR, AND BURKEY, LLOYD 1925 Modifying *Rhizobium radicicolum*. *Soil Sci.* 20: 143–147.

(2) GARMAN, H., AND DIDLAKE, M. 1914 Six different species of nodule bacteria. Ky. Agr. Exp. Bul., 184: 343–363.

(3) SEARS, O. H., AND CARROLL, W. R. 1927 Cross inoculation studies with cow pea and soy bean nodule bacteria. *Jour. Bact.* 13: 55.